FORMATION OF DIFFUSION COATINGS ON IRON AND STEEL: 3 ALUMINIUM, CHROMIUM AND ZINC COATINGS

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ABSTRACT

The present paper is the last part of a three part series dealing with metallic diffusion coatings for the protection of iron and steel. In this part special reference is made to the application methods, the composition and structure, the physical properties, and the corrosion and oxidation resistance of aluminium, chromium and zinc diffusion coatings. Suggestions are made for future studies, of the deposition and performance, of diffusion coatings on iron and steel substrates.

INTRODUCTION

Aluminium and zinc are readily obtainable in wrought and cast form, in a range of alloys, and their cost is moderate. On the other hand, chromium and its alloys, are difficult to manufacture, suffer from brittleness and poor resistance to thermal shock, and the element is costly. However, the iron-chromium alloys are commercially available and are the basis of the well-known stainless and heat-resistant steels. Alloys of this nature are formed at the surface of the basis steel by the chromium-diffusion coating process (chromizing).

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The net result is an article which can be of simple, or complex, form possessing the surface properties of a considerably more expensive material and which can be processed within close dimensional tolerances. Iron.aluminium alloys are also very heat resistant but require further development before they are suitable as constructional metals. The largest single use of zinc is in the form of coatings, more than half of the total production being used for the protection of other metals.

Aluminium and zinc are of relatively low melting point (657° and 419,5°C) so that both metals can be readily applied by hot-dipping. Cementation coatings are also produced at reasonably low temperatures. Chromium can be diffused into a surface by the cementation process but an activating agent is required if it is to be carried out at technologically available temperatures.

Although aluminium and zinc are soft ductile metals (unlike chromium) the intermetallic compounds formed with iron are brittle and hard in all cases. Cementation coatings are therefore particularly useful where a moderate degree of abrasion resistance is required.

Aluminium and chromium are both passive metals in the true sense. Zinc exhibites a good corrosion resistance and this is attributed to the formation of an adherent, protective, layer of corrosion products (this also may be considered as a form of passivity). Chromium, at concentrations greater than 12 per cent, endows passivity to its alloys with iron and these alloys are cathodic to steel. Under most conditions, both aluminium and zinc are anodic to steel as are iron-zinc alloys. Iron-aluminium alloys, however, are cathodic and in this

respect are similar to iron-chromium alloys. The corrosion resistance of steel is increased by alloying with aluminium or chromium; the increased is marked with the latter. The addition of zinc decreases the corrosion resistance of steel although in many cases a protective layer of corrosion products leads to an apparent decrease in the corrosion rate.

Although similar in their corrosion resistance, aluminium coatings are preferred to zinc coatings for marine and industrial environments; they are however less suited to alkaline conditions. Chromium is only used decoratively in conjunction with nickel or copper undercoats. The general properties of the diffusion (alloy) coatings can be summarized in the following manner:

Coatings	Property		
	Corrosion	Oxidation	Abrasion
Iron - Zinc	Moderate	Moderate	Slight
Iron - Aluminium	Moderate	Good	Slight
Iron - Chromium	Good	Good	Good

In this paper we compare and describe relevant aspects concerned with aluminium, zinc and chromium diffusion coatings that are used extensively for the protection of iron and steel. But it is not our intention topresent a comprehensive bibliography particularly where the literature is already prolific and readily available (e.g. hot-dip galvanizing).

ALUMINIUM COATINGS

Application methods

Methods available for coating steel with aluminium (Table 1) in decreasing order of industrial importance are [1, 2]:

i) Metal spraying
ii) Cementation
iii) Hot-dipping
iv) Cladding
v) Electrodeposition
vi) Vapour deposition

Nowadays, increasing emphasis is being placed upon vacuum and powder-coating techniques particularly for coated-steel strip [3, 4]. Metal spraying [5-10] is probably the most versatile technique but the cost per unit area is high although the initial capital outlay is relatively small. It is widely used as a basis for painting as well as a protective coating on its own [11]. The cementation and hot-dip methods are amenable to mass production; the batch-operated processes are limiting in size. The high temperature involved in the formation of aluminium diffusion

TABLE 1

Methods used for the application of aluminium coatings

Method	Temperature (°C)	Thickness (mils)	Deposition rate (mils/h)	Structure of the coating	Remarks
Cementation	850-950	5-40	0.5-1	Basically delta solid solution (25% Al) with an outer scale of alumina (Al_2O_3)	Pack process, often in two stages, known as calorizing
Cladding	200-530	5-10% of substrate	—	Pure, dense, surface layer of aluminium with a small amount of alloying at the interface	Rolled or drawn products only
Hot-dip	700-750	0.5-3	20-70	Outer layer of aluminium; inner alloy-layer of one or more Fe-Al compounds	
Metal Spray	Ambient	2-20	—	Porous structure (density approx. 2.3g/cc) with small content of alumina	B.S. 2569 Powder, wire or molten-metal process. Can be diffusion annealed at 600°-1000°C

coatings can affect the mechanical properties of the substrate, and warpage may also be incurred. These methods are listed in Table 1 with an indication of the typical thickness of aluminium applied in each case.

a) Pack and cementation processes

Calorized coatings are produced in a manner similar to that used in sherardizing and were first described by Allison and Hawkins [12] in 1914. The article to be coated is first cleaned thoroughly, dried, and then sealed in an air-tight retort with the calorizing mixture; this usually contains powdered aluminium (or a ferro-aluminium alloy), alumina and ammonium chloride (1-5 per cent). The addition of a halide not only activates the reaction but also facilitates the initial reaction by acting as a flux. The container is then heated to promote diffusion, for example at 800°-950°C for 2-24h. If the mixture is tumbled (c. f. sherardizing) [13] a treatment time of 4-6h suffices. In the latter case (high-flux treatment) a high aluminium concentration is maintained at the surface, and the coating (0.001-0.006 in.) is porous and brittle with a high surface aluminium concentration (e. g. 50-60 per cent). A secondary heat treatment (815°-980°C for 12-48h) results in a thick coating (0.025-0.040 in) of increased ductility; the surface aluminium concentration is decreased to about 25-35 per cent. The coating thickness obtainable by this method is shown in Fig. 1 as a function of both time and temperature.

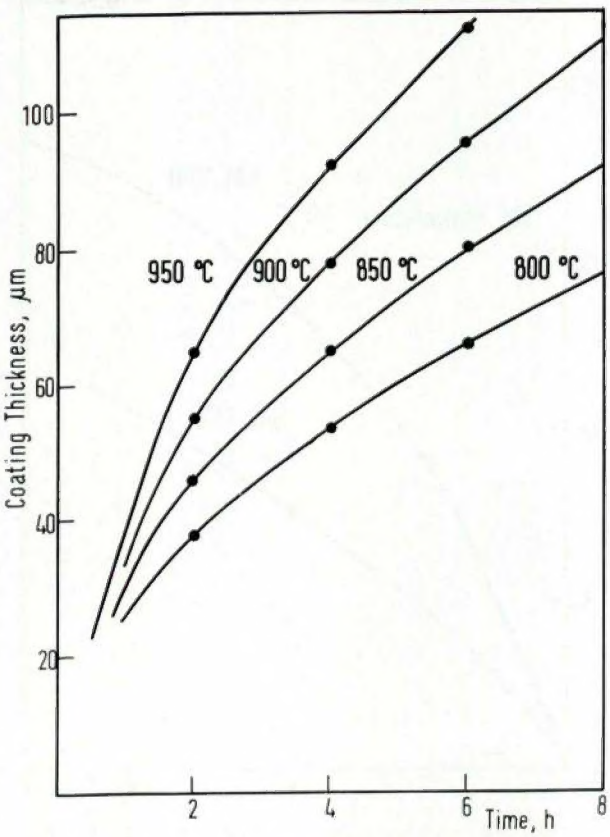

Fig.1 Aluminium cementation coating-effect of process time and temperature on thickness of coating (53).

b) Hot-dipping

Hot-dip aluminizing consists essentially in the surface pretreatment of the steel followed by immersion in a bath of molten aluminium at 705°-760°C [14-16]. There are many patents covering surface pretreatment for not only must the steel be clean but it must also be preheated, and protected from oxidation, before immersion in the hot-dipping bath. Successful techniques have utilized copper wash coatings, controlled reduction, and both molten and gaseous fluxing.

Iron and aluminium alloy readily being completely miscible in the molten state, although the solubility of iron in aluminium at 640°-650°C is only 0.06 per cent. The coating comprises an outer layer of virtually pure aluminium and an interfacial zone of iron-aluminium intermetallic compounds. The thickness of the alloy-layer depends on the temperature and time of imersion, and the alloying elements present in the steel or aluminium. The iron-aluminium compounds, particularly $FeAl_3$, are brittle and if satisfactory mechanical properties are required the thickness of the alloy-layer should not exceed 0.0004 in. [17]. Although this is of litle consequence for batch-dipped items, wich do not require subsequent forming, excessive alloy formation also results in iron contamination of the bath which gives rough coatings caused by the inclusion of dross ($FeAl_3$) particles.

In practice, control of alloy formation during hot-dipping is effected by preheating the steel (thus minimizing the immersion time), pre-coating the steel with either metallic (e. g. copper) or non metallic (e. g. phosphate or organig coatings) films, decreasing the bath temperature, and by alloying additions of silicon (3-9 per cent) to the bath. The factors controlling the thickness of hot-dip coatings are illustrated by Figs. 2-5. Hot-dipped aluminium coatings are often given a secondary heat treatment particularly when good heat resistance is required (see Diffusion Coatings by Heat Treatment).

Alloying elements but also the surface appearance and physical properties of the coatings [18]. Molybdenum, manganese, zinc and sodium improve the wettability of the coating; in addition sodium promotes even distribution of the aluminium-silicon eutectic thus increasing the ductility of the coating. Beryllium, in addition to its restrictive effect on the formation of the alloy-layer also reduces the flexibility of the coating [19], prevents discoloration of aluminium-silicon coatings, and reduces oxidation at the surface of the bath.

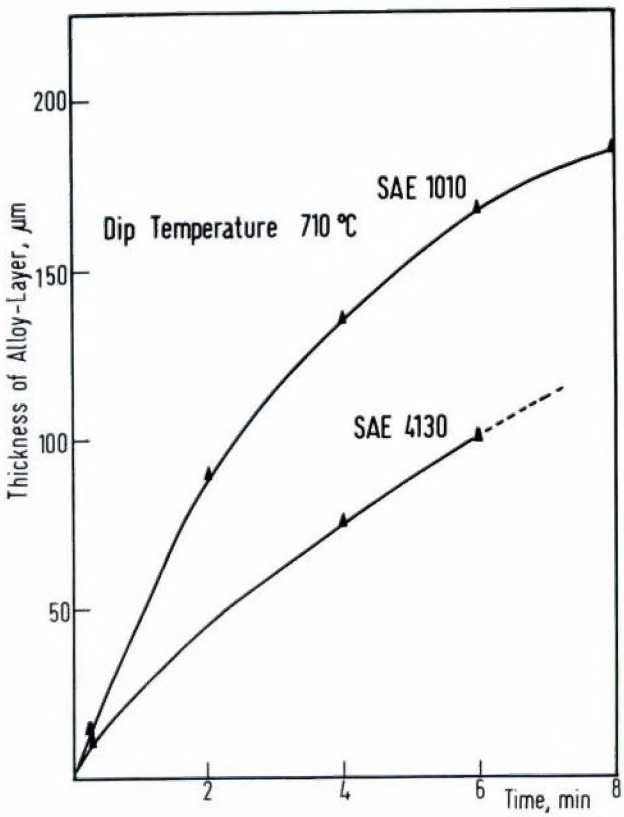

Fig. 2 Hot-dip aluminizing - effect of immersion time on thickness of alloy-layer (31).

c) Miscellaneous methods

Cladding of steel sheets with aluminium has been in commercial production [20] for more than two decades and is of particular use in severely corrosive environments. The work, by Cook and Levy [21], demonstrates the importance of surface pretreatment, pressure and heat treatment. As an example, the required bonding temperature was found to be an inverse function of pressure (e. g. the same bonding strength could be attained at either 20,000 p.s.i. - 400°C or 30,000 p.s.i. - 345°C); subsequent annealing could double the bond strength. The sheets are pre-roughened by rotary wire-brushes, rolled first at 535°-550° for 10-15h. A temperature as low as 230°C can be used if the steel has been initially silver-plated.

Casting of aluminium around steel components has been used where high strength, corrosion resistance, good heat transfer, electrical condutivity, etc. is required of a fabricated article. The surface is first prepared by the formation of an iron-aluminium intermetallic after which the aluminium can be cast. Good adhesion is obtained in this manner but the coating thickness is limited by the difference in expansion coefficients.

Electrodeposition of aluminium is severely limited by the necessity to use molten salt baths or anhydrous organic electrolytes.

Although aluminium coatings can be obtained by deposition from vapour sources (e. g. aluminium chloride, organo-aluminium compounds or physical vapour deposition) the use of such techniques only recently has been exploited commercially to some large extent [22-25].

d) Diffusion coatings by heat treatment

After the application of the aluminium coating to the steel substrate heat treatment is often given. Coatings resulting from vacuum deposition, electroplating, electrophoretic application, cladding and powder-coating techniques are annealed to provide adhesion by diffusion-alloying [26].

The adhesion of sprayed-metal coatings is considered to be purely mechanical. Annealing (spray-fusing) of these coatings, at 750°-950°C for 1/2-5h, not only improves adhesion but the formation of iron-aluminium compounds gives increased oxidation resistance. To prevent excessive oxidation of the coating, annealing should be done in an inert or reducing atmosphere; alternatively the coating can be sealed by the application of calcium hydroxide, sodium silicate, or bitumen coatings. The use of a cadmium-(0,75%) bearing alloy is also recommended as this promotes diffusion.

Hot-dipped coatings are also annealed prior to service where oxidation resistance is required.

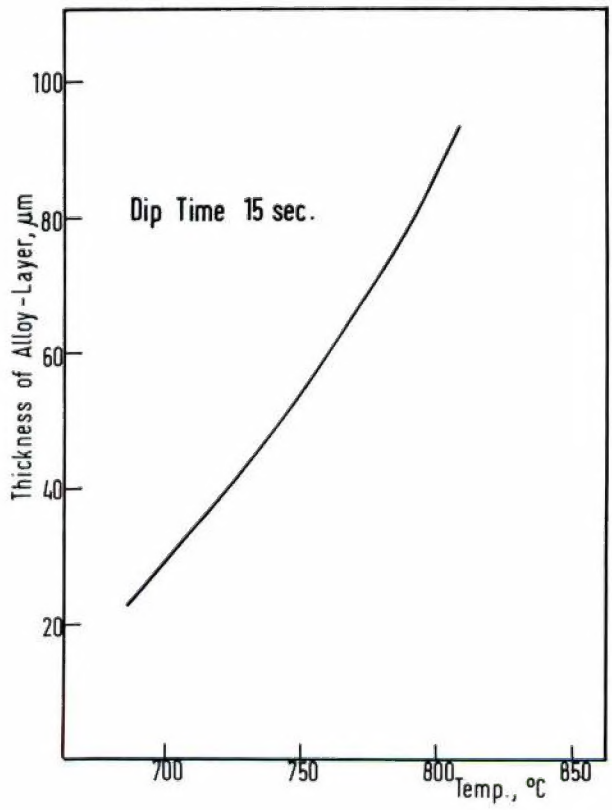

Fig. 3 Hot-dip aluminizing - effect of temperature on the thickness of the alloy-layer (166).

Successful treatment requires maintaining as high a surface concentration of aluminium as possible, but should this exceed a critical value or the concentration gradient be two steep, the resulting coating will have a tendency to spall in service due to thermal stresses.

Composition and structure

Alloying of aluminium and iron generally starts at about 480°C although excessive work-hardening of the substrate can result in significant diffusion occurring at temperatures as low as 300°C. In the temperature-range of diffusion-coating processes alloying proceeds rapidly and, on the basis of the Fe-Al equilibrium diagram, the alloy-layer could consist of one or more of the following phases; α-solid solution, the zeta phase $FeAl_2$, eta-Fe_2Al_5, and theta-$FeAl_3$.

The composition of a cementation coating resulting from the high-flux treatment is basically $FeAl_3$; a subsequent heat treatment or the low-flux process results in the formation of the α-solid solution generally with a surface layer of alumina (Al_2O_3). The structure is of a columnar nature.

Coatings produced by conventional hot-dipping are duplex, with an outer layer of essentially pure

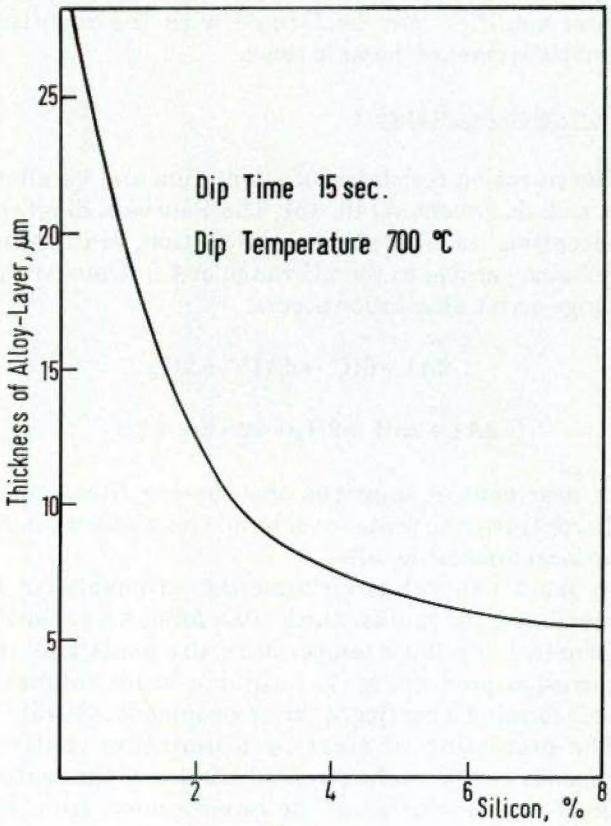

Fig.4 Hot-dip aluminizing - effect of silicon on the thickness of the alloy-layer (166).

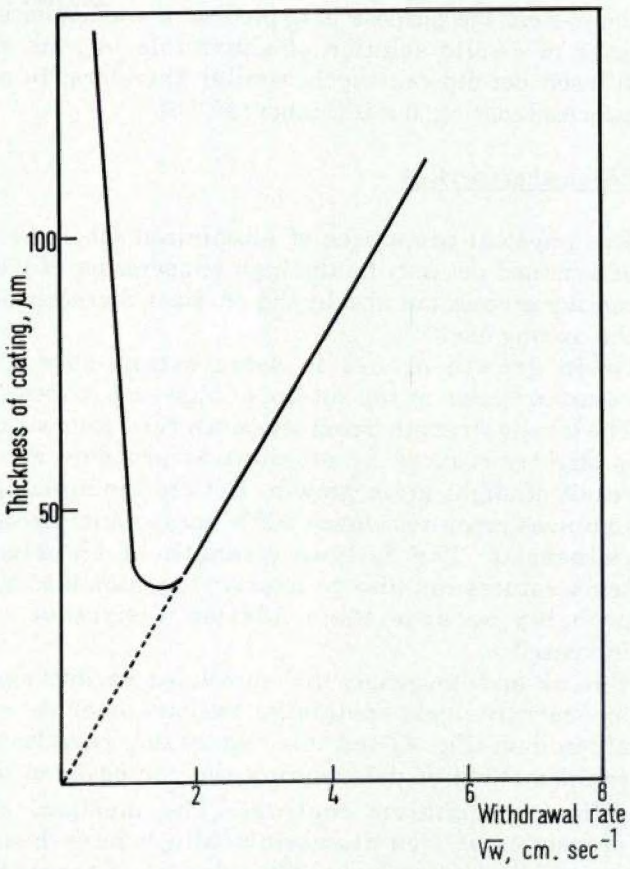

Fig.5 Hot-dip aluminizing - effect of treatment speed on thickness of coating (167).

aluminium (solubility of iron 0.06%) and an interfacial alloy-layer. The alloy-layer resulting from a bath of pure aluminium is wholly of Fe_2Al_5 [27,28] and is characterized by its pallisade structure. Elements that decrease the rate of formation of the alloy-layer (notably silicon, beryllium, chromium, copper and titanium) result in the preferential formation of $FeAl_3$ [29] which acts as a barrier and restricts the diffusion process. The presence of other intermetallic compounds in the alloy-layer has also been reported e. g. $FeAl_2$ and Fe-Al-Si phases [30]. Steels of different carbon content react differently; high-carbon steels are decarburized [31], although not to such an extent as that produced by chromizing, and the alloy-layer comprises Fe_2Al_5 and Al_4C, probably with ternary carbides at the interface [32]. In cast iron there is no decarburization but fine carbide precipitates are apparent [33]. When present as a layer the carbides can inhibit formation of the alloy-layer (c. f. chromizing); they also decrease the corrosion resistance of these coatings as the carbides are easily hydrolysed.

The alloy-layer of coatings formed by a secondary heat treatment in order to provide an interfacial bond is similar to that obtained by hot-dipping, but much thinner, and is basically Fe2Al5. Where heat treatment is given to increase the heat resistance of

the system the purpose is to produce a single-phase layer of α-solid solution of aluminium in iron; a diffused hot-dip coating is similar therefore, to a calorized coating, but is thinner [34, 35].

Physical properties

The physical properties of aluminized steels are determined not only by the high temperature of the coating process but also by the physical character of the coating itself.
Grain growth occurs to some extent as does decarburization at the surface of high-carbon steels. The tensile strength (room temperature) of mild steel is slightly reduced by aluminizing probably as a result of slight grain growth. Hot-dip aluminizing improves creep resistance while spray-aluminizing reduces it. The fatigue strength at elevated temperatures can also be improved by aluminizing, probably because the oxidation resistance is increased.
Hanink and Beogehold [31] correlated hardness of low-carbon steels containing various amounts of aluminium (Fig. 6) and this relationship provides a rapid method of determining the composition of diffused-aluminium coatings. The mechanical properties of iron-aluminium alloys have been investigated extensively [36] and a lot of research

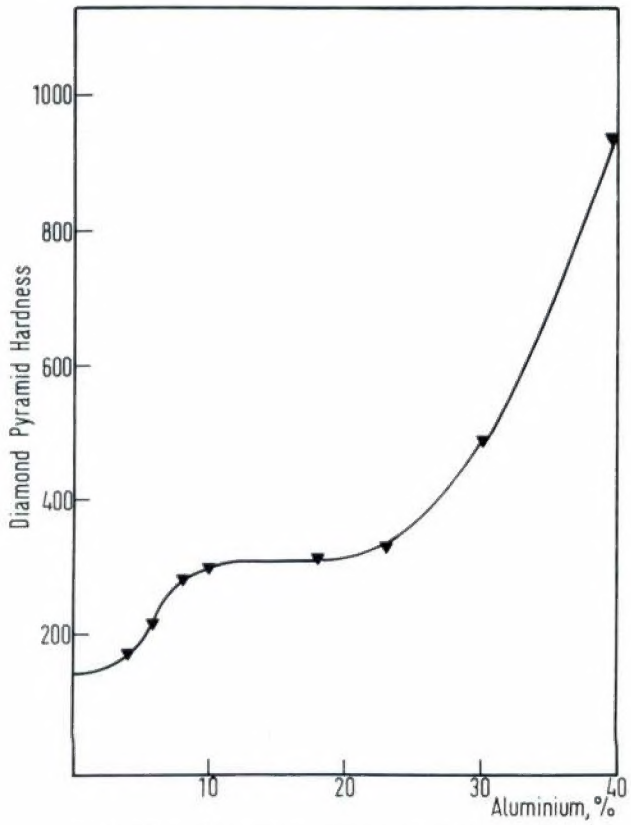

Fig 6 Effect of aluminium content on the hardness of an 0.1% carbon steel (31).

[37, 39] is concentrated on the production of ductile materials. A brittle coating is limited in use by the tendency to crack and-or, flake in service, thereby exposing the substrate to the environment. The severity of such effects will be determinated not only by the ductility but also the thickness of the coating. A calorized coating, although composed of the relatively soft α-solid solution will not stand severe deformation (greater than 5% elongation) but can be hot-worked, without severe damage by cracking. A coating produced by hot-dipping, however, can be formed (e. g. 3d-bend) particularly if growth of the alloy-layer has been restricted. Unlike galvanized coatings, aluminium coatings on sheet steel tend to fail at the alloy-aluminium interface at the surface under compression.
The mechanical properties of aluminium-sprayed steel remain substantially unimpaired except for a slight loss in fatigue strength due to the notch effects caused by the preliminary grit-blasting. The fatigue properties of aluminized steels at normal temperatures may be affected if the steel is particularly notch sensitive, especially with calorized coatings.
Any of the standard welding methods can, with care, be used for joining aluminium-coated steel, spot and seam welding being especially desirable thereby keeping coating damage to a minimum. However care should be taken to avoid conditions where brittle intermetallics may be formed with the resulting embrittlement of the weld zones.

Corrosion resistance

The corrosion resistance of aluminium and its alloys is well documented [40, 45]. The Pourbaix diagram, accepting its limitations, shows that aluminium remains passive in the pH range of 4-9. Outside this range active dissolution occurs:

$$2Al + 6H^+ \rightarrow 2Al^{3+} + 3H_2$$

$$2Al + 2OH^- + 2H_2O \rightarrow 2AlO^-_2 + 3H_2$$

In near-neutral solutions the passive film can be disrupted by the presence of halide ions which can set up local bimetallic cells.
In most neutral environments, atmospheric or immersed, the rate of attack often follows a parabolic form (c. f. low 'high temperature' dry oxidation), the corrosion products (e. g. insoluble basic sulphates etc.) forming a barrier to the environment [44, 45].
The protection of steel by aluminium coatings depends partly on the physical barrier of the coating itself (i. e. exclusion of the environment from the substrate) and partly on sacrificial action. The extent of the latter depends on the environment, the

aluminium composition [46] and the area of steel exposed; for example, in the presence of chloride ions (e. g. immersed in sea-water) aluminium would be fairly active and the low-resistivity electrolyte would ensure satisfactory protection of the steel by sacrificial action.

In order to obtain barrier-protection an adequate thickness of aluminium is required to enable the protective film of corrosion products to form. Because of the tendency to pitting under burried conditions only thick coatings (0.010-0.015 in) are recommended for this aplication and, in general, the overall protection increases with the thickness of aluminium. The corrosion resistance of the iron-aluminium alloys, [36, 39] which are generally cathodic to the steel substrate, is superior to that of mild steel although there is a tendency to pitting. Atmospheric exposure tests [43, 47] on calorized and hot-dipped coatings show that the latter offer substantial protection to a steel substrate, for many applications.

The use of silicon in hot-dipping baths does not detract from the corrosion resistance but does cause premature darkening on the surface by weathering. On the other hand the use of a copper coating on the steel strip (or as an addition to the bath) introduces the danger of an increasing copper content in the coating with a corresponding decrease in corrosion resistance.

The field of application for aluminium-coated steel is dictated by the nature of the coating; aluminium coatings for corrosion resistance and iron-aluminium coatings (i. e. diffusion coatings) for oxidation resistance.

Oxidation resistance

Aluminium itself is relatively oxidation resistant as is steel, but melts at about 650oC; diffusion-alloying with iron commences at temperatures as low, as 300o-480oC. Is has been shown [36, 48, 49] that the oxidation resistance of iron increases with aluminium content (Fig.7), a concentration of 8-10% being adequate to reduce oxidation at 1000o-1100oC to an insignificant amount [44].

Obviously, the physical properties of the substrate must also be adequate not only for structural reasons but also to minimize spalling.

The resistance is attributed to the formation of alumina [50] although a spinel $FeO.Al_2O_3$ may also be formed. At these temperatures any iron oxides present will be reduced by the aluminium to the metallic state.

Extensive data is available on the oxidation (or scaling) resistance of aluminium-coated steel. There are, basically two factors to consider:

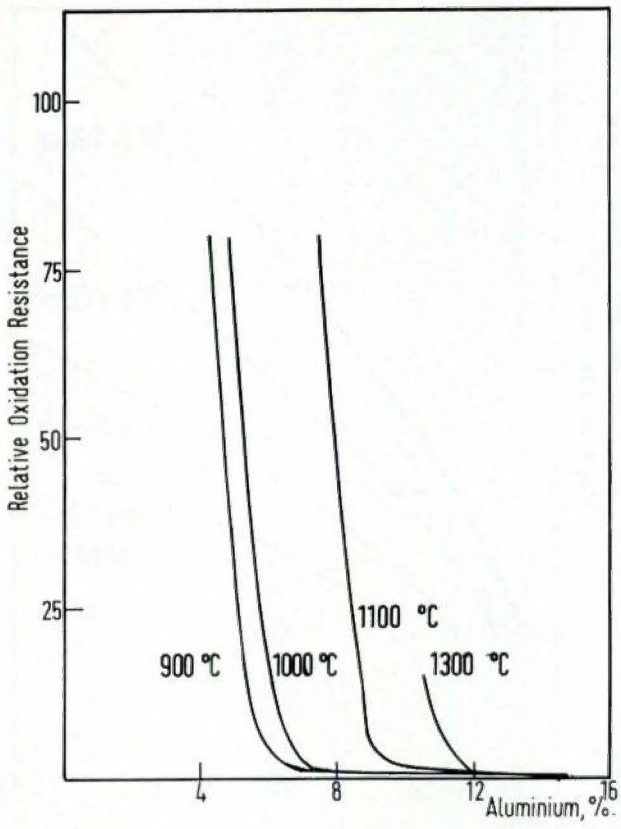

Fig. 7 Oxidation resistance of iron-aluminium alloys (36).

i) The form of coating that is most resistant to spalling when exposed to high-temperature service.
ii) The effects of oxidation and secondary diffusion wich both tend to deplete the surface of aluminium.

Up to 500oC aluminium coatings may be used in the as-applied condition but for service at higher temperatures a subsequent diffusion treatment is recommended for hot-dipped coatings [31] and sprayed coatings [11]; calorized coatings do not require a diffusion treatment. A coating thickness of 0.012 in. is recommended as the desirable minimum for high-temperature service.

Above 900oC the life of aluminized steel is limited, although extended over that of the bare metal (e. g. at 900o-980oC the life is increased 20 times, 980o-1000oC the life is increased 5 times). Below 750oC the life of aluminized steel components is considered to be indefinite. Results obtained between 750o-900oC are conflicting, although the presence of silicon has been shown to be detrimental (Fig. 8) at all temperatures. Aluminium-coated steel has also been shown to be particularly resistant to sulphurous atmospheres [44, 51, 52]. In this respect it is particularly useful for the protection of the heat-resisting grade of steels.

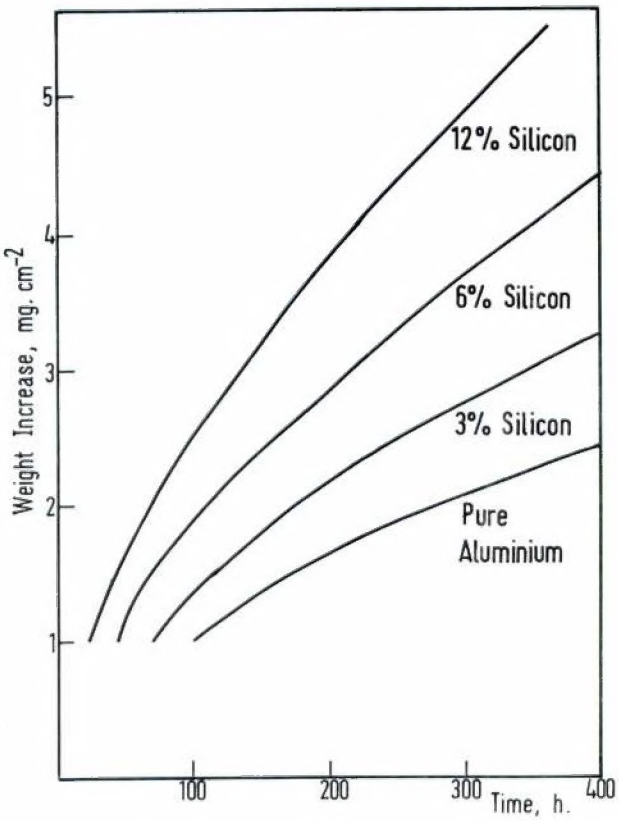

Fig. 8 Effect of silicon on oxidation rate of aluminium at 700 °C (168).

CHROMIUM COATINGS

Application methods

Until the years 70 most chromium coatings have been applied (Table 2) either by electrodeposition or chemical vapour deposition. In the strip-coating field vacuum [54, 55], powder-coating [56-58], and electrodeposition have been investigated extensively [59] since steel having a thin flash-coating of chromium can compete successfully with tin-plate.

Electrodeposition is satisfactory for many applications. The deposits obtained are of two main types:

i) Decorative plate

ii) 'Hard' (engineering) chromium plate

Thin coatings of chromium [60] are applied over another electrodeposited layer, usually nickel or copper, as a decorative non-staining finish; these thin (0.01 mils) layers are porous. Hard chromium plating is used in order to take advantage of the high hardness and wear resistance, or the low coefficient of friction, of such deposits. Chromium electrodeposits are not suitable for use at high temperatures as the stresses resulting from differential thermal expansion at the interface are severe and often lead to spalling particularly when subjected to thermal cycling.

Chromium diffusion coatings are superior in this respect because of the adhesion provided by metallurgical bond. Because of its commercial interest a number of important developments are reported in the patent literature; Mortimer [61] reviewed the progress made up to 1962.

Historically, chromizing was first achieved by Kelley [62] in the form of a cementation process, but a major disadvantage inherent in his method was the high temperature (1300°C) that is required. Weber [63] and Marshall [64] overcame this problem by using a halogen carrier compound the function of which was

TABLE 2

Methods used for the application of chromium coatings

Method	Temperature (°C)	Thickness (mils)	Deposition rate (mils/h)	Structure of the coating	Remarks
Electrodeposition	20-85	0.01-20	0.2-0.5	Essentially pure, although cracked coating	Thin coatings (0.01 mils) are porous and are used for decorative and protective purposes over copper or nickel undercoats
Vapour	900-1100	1-6	0.2-0.6	Solid solution of chromium in iron	Generally a pack process combining cementation and chemical vapour deposition

to provide a volatile source of chromium at the substrate surface. By these means temperatures were reduced to the order of 1000°C. The various processes that have been devised for chromizing metals by vapour deposition may be summarized as follows:

a) Chromizing is carried out by a two-stage process being the production of chromous chloride followed by the action of the activator on the metal surface in the presence of a reducing atmosphere [65], e. g. hydrogen or a mixture with hydrogen chloride is passed over anhydrous $CrCl_2$ (or Cr powder) at 850°-1000°C and thence over the steel substrate at 1000°-1200°C for a period of several hours.

b) The process can be carried out by pack techniques e. g. the sample is packed in a mixture of powdered chromium (or ferro-chrome) and ceramic granules are heated at 850°-1000°C in a stream of hydrogen with hydrogen chloride (or chlorine) for several hours [66]; alternatively the activator can be introduced in-situ via the ceramic granules (i. e. saturated with $CrCl_2$) or as amonium fluoride or ferric chloride etc. [67].

c) Chromizing has also been studied [68, 69] at reduced pressures (20 torr); in this way, the partial pressure of the activator is increased although it is doubtful whether this advantage outweighs the inherent technological difficulties.

d) Samuel [70] has patented a high-frequency heating process described in more detail by Lockington [71] and also investigated by Russian workers [72, 73]. Diffusion rates were increased by this means with a consequent decrease in process time.

e) Salt-bath chromizing has also been investigated [68, 74, 75] and extended by the 'metalliding' process [76].

f) Low-temperature (300°-650°C) deposition by reduction or pyrolysis of other chromium compounds (e. g. carbonyl, dicumene, etc.) has only been partially successful [77].

Carbon is undoubtedly the element which exerts the most marked influence on the chromizing of steel and its effect is two-fold: a) it produces a decarburized layer in the substrate surface and b) the carbide layer, so formed in the coating, is a barrier to diffusion thus limiting the coating thickness. Four methods of overcoming the effect of carbon have been detailed by Samuel and Lockington [78]:

a) The use of low-carbon steels
b) Decarburization prior to chromizing
c) Addition of carbide-forming elements (e. g. vanadium, molybdenum, titanium, etc.) to the steel
d) The diffusion of carbide-forming elements during chromizing together with the chromium [79]

Special steels (Inkromstähle [65]) have been developed in Germany for the chromizing process containing such elements as titanium, chromium and vanadium or molybdenum.

Other elements can influence the formation of the coating by altering the rate of diffusion or modifying the surface reactions. Sulphur and phosphorous have a poisoning effect on the chromizing media: most other elements influence the rate of diffusion by virtue of their effect on the stability of the metallic phases present.

The coating thickness increases with temperature and duration of treatment. The average thickness of the coating can be determined by dissolving the core in warm nitric acid (10-20 vol. %) and determining the weight of the remaining coating. Under similar conditions of formation the thickness of the coatings decrease with increasing carbon content of the steel [80]. The data obtained from the various different chromizing processes is very similar (typical results are illustrated by Fig. 9) with the exception that salt-

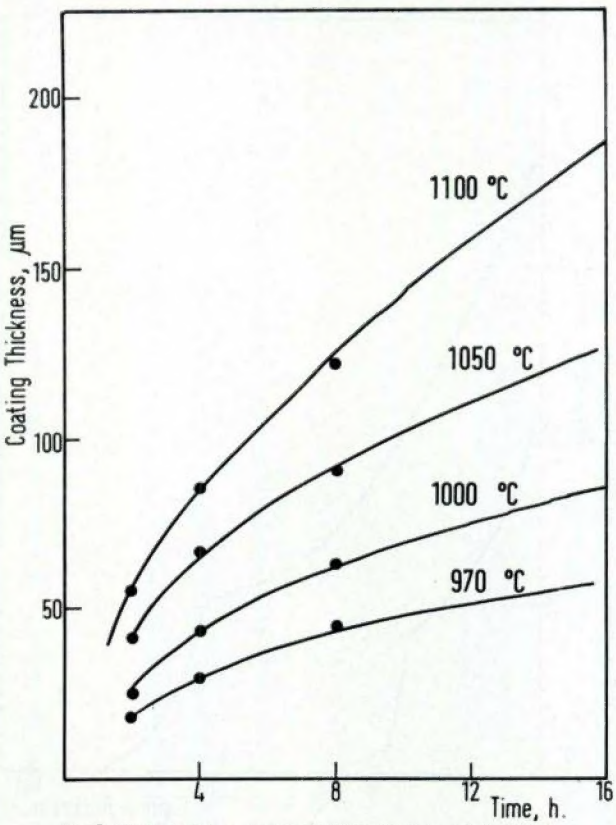

Fig. 9 Chromizing - coating thickness vs. time and temperature (169).

bath chromizing tends to produce thinner coatings. Typical thicknesses of chromized coatings are 0.003-0.005 in. on low-carbon steels and 0.005-0.001 in. on medium-high carbon steels although values up to o.oo15 in. have been reported [81-84].

Composition and structure

Iron and chromium form a solid solution over the whole composition range although there is a phase transition ($\gamma = \alpha$) at about 12-13% chromium at temperatures around 825oC. In chromium diffusion coatings that have been formed at temperatures higher than this a phase boundary can be clearly seen; a typical concentration gradient , which agrees with a diffusion mechanism, is shown in Fig. 10.
The structure of the chromized coating has been examined in detail; Menzies and Mortimer [80] have studied the chromizing of iron and plain-carbon steels (up to 0.7% carbon). There is very litle variation of structure with duration of treatment, but considerable differences with carbon content of the steel and process temperature. The observed structures can be classified in two groups:

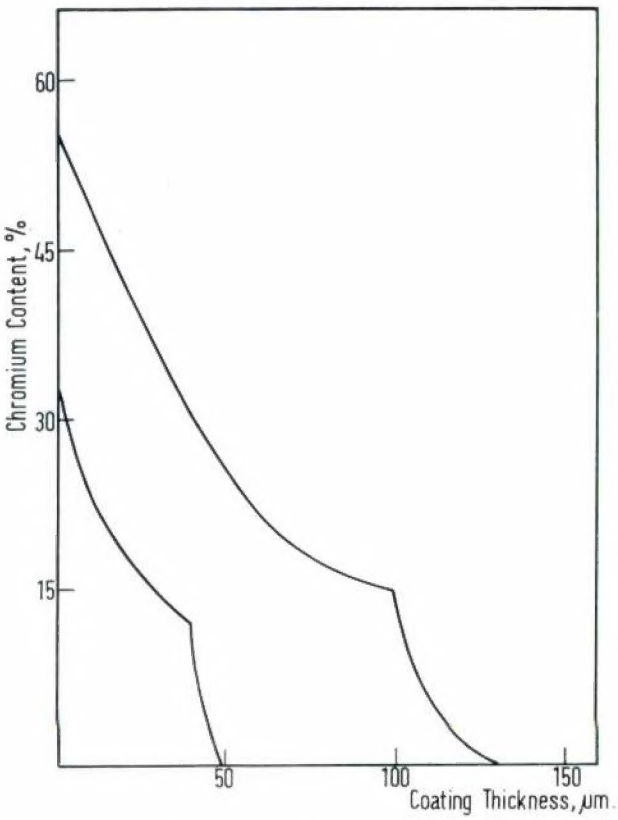

Fig. 10 Chromizing - chromium distribution in a coating on an 0.1% carbon steel (80, 88).

a) Low carbon steels (<0.2%).
b) Steels with a carbon content greater than, or equal to, 0.2%.

On iron and low-carbon steels there is a considerable variation in structure with chromizing temperature, and at 950°C the coating is mainly comprised of columnar ferrite chrystals. A lamellar structure, mainly ferrite+carbide, becomes apparent as the temperature is raised, with a thin layer of martensite at the substrate-coating interface on specimens of higher carbon content (0.16%). At temperatures greater than 1200°C the coatings consist mainly of columnar grains of ferrite with a layer of martensite (approximately 1/3 to 1/4 of the total thickness) at the interface.
The structures of the coatings formed on high-carbon steels between 950°-1125°C consist of ferrite crystals with a carbide layer near the surface. On lower carbon steels (0.4%) these carbides are present mainly in the grain boundaries, but a higher carbon content results in the formation of lenticular grains laying parallel to the surface. The carbides have been isolated and identified as $(Fe, Cr)_7C_3$ and possibly $Cr_{23}C_6$. The concentration of carbide in the coatings was found to be proportional to the carbon content of steel.
The average chromium content varies with both time and temperature of treatment but most markedly with the carbon content of the steel. At low carbon contents average chromium concentrations of 19-27% are noted increasing to 40-65% for the high carbon steels (0.7%) [85-87].
The distribution of chromium is ilustrated by Fig. 10 which shows that the chromium content at the surface is usually about 30-60% [88]. The actual value will depend on the type of process, the treatment temperature and time, and the composition of the substrate. Values as diverse as 27 [89] and 96% [81-83] have been found.

Physical properties

The hardness and ductility of a chromized surface is dependent mainly upon the carbon content of the substrate [67, 90]. In the range 0.16-0.80% carbon there is a linear relationship between carbon content and the hardness of a coating on a low-carbon steel is similar to that of the core metal. Coatings on low-carbon steel are ductile although severe reductions [89] (>45%) may induce rupture. Fabrication and jointing techniques for chromized steel have been discussed in detail by Vaccari [89], Samuel and Lockington [91], Melloy and Brubaker [92], and Shin and Yin [93].
Chromized coatings on carbon steels (e. g. >0.3% carbon) are extremely hard and brittle. Samuel [94]

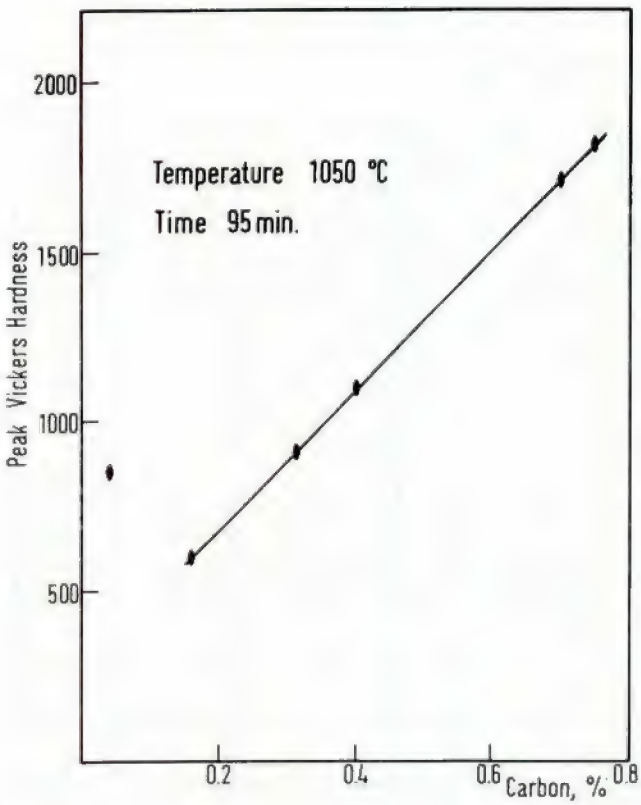

Fig 11 Microhardness of a chromized coating vs. carbon content of steel (80)

has suggested that chromized medium-carbon steels (0.3-0.45%) are suitable for applications requiring good wear and abrasion resistance, and high-carbon steels give coatings with a very low friction coefficient. The surface hardness of chromized coatings can, however, be increased with subsequent carburizing [95] or nitriding [96].

Chromizing has litle effect on the normal mechanical properties of the basis steel in so far as these are affected by the conditions of the process; typical results have been published [89, 97, 98]. Sully [99] has suggested that the fatigue resistance of the metal may be adversely affected by the presence of any cracks in the chromized surface. This will obviously be dependent on both the type (and thickness) of coating as well as the substrate [100]. Bollenrath and Broichhausen [97] have investigated the fatigue properties of chromized bolts and found that, in a corrosive environment, there was no reduction in their fatigue strength although that of the untreated bolts was markedly reduced. Chromium electrodeposits are known to reduce the fatigue strength of high-tensile steels [101] although hydrogen embrittlement, stress in the chromium deposit, and the crack density (of the deposit) have all been suggested as initiating factors. Chromized coatings are free from these effects and in this respect should therefore be superior to chromium plating.

Corrosion resistance

The corrosion resistance of a chromized mild steel is generally considered [102-106] to be similar to that of a 30% chromium steel; Burns and Bradley [107] consider that the chromized material is more resistant to oxidation at elevated temperatures while the chromium steel is better for wet-corrosion resistance. Samuel and Lockington [78] suggest that heterogeneities such as carbides, sigma phase, porosity and inclusions decrease the corrosion resistance particularly in strong electrolytes.

Heterogeneities such as these would probably result in active-passive cells being set up on the surface and consequent localised corrosion. A passivation treatment, in nitric acid (e. g. 20%) has been proposed [98] to overcome the slight rust staining sometimes associated with the use of chromized steels in environments such as marine atmospheres.

Data in tabular form has been presented by several authorities [78, 94, 98] and is summarized below in Tables 3 and 4.

The remaining information in this section has been collected from many sources and is classified as resistance to atmospheric conditions, acids, alkalies, salt solutions (including waters) and miscellaneous media.

a) Atmospheric conditions

Chromized steel is suitable for use, under both damp or saline conditions, [108] being unaffected after exposure to a 100% relative humidity for 500 hours at 45°C [89], and only showing slight attack at normal temperatures when the environment was saturated with sulphur oxides, [81-83]. It shows good resistance to most types of atmospheres [78], e. g. marine, industrial, and other polluted (SO_2,CO_2 and

TABLE 3

Corrosion resistance of chromized steel compared with some other materials (94, 98)

Environment / Material	Humidity (100% R.H. - 40°C)	Water (95°C)	Alkalies	Sodium hydroxide (1.25%)	Organic acids	Acetic acid (20%)	Sulphuric acid (20%)	Hydrochloric acid (7.5%)	Nitric Acid (20%)	Brines	Salt Fog (A.S.T.M. - B117 - 57T)
Chromized steel	1	1	1	1	1	1	4	4	1	2	2
Galvanized steel	2	2	3	3	4	4	4	4	4	4	3
Aluminized steel	2	2	3	3	2	2	4	4	1	4	3
Bare steel	3	3	2	2	3	3	4	4	4	4	4
Stainless steel (17 Cr)	1	1	1	1	1	1	4	4	1	2	2

Very good 1
Good 2
Medium 3
Poor 4

TABLE 4

Corrosion resistance of chromized steels (78)

Environment / Material	Atmosphere	Alkali and soap water	Tap water	Salt water	Dilute nitric acid	Dilute hydrochloric acid	Dilute sulphuric acid	Bleaching solutions	Fruit juices	Milk products	Oils and petroleum	Oxidation at high temperatures	Combustion gases (furnaces)	Combustion gases (IC engine)	Steam at high temperature	Molten cyanide	Molten activated cyanide	Chloride salt bath	Molten lead, aluminium and zinc
Pure iron	1	1	1	1	1	3	4	2	1	1	1	1	1	1	1	1	1	1	1
Low carbon steel (0.15% carbon max.)	1	1	1	1	1	3	4	3	1	1	1	1	1	1	1	1	1	1	1
Low carbon steel (0.25% carbon max.)	1	1	1	2	1	4	4	4	2	1	1	1	1	1	1	1	1	1	1
Medium carbon steel (0.25 to 0.6% carbon)	1	1	1	2	1	4	4	4	2	2	1	1	1	1	1	1	1	2	1
High carbon steel (0.6 to 1.2% carbon)	1	1	1	2	1	3	4	4	2	2	1	1	1	1	1	1	1	2	1
Homogeneous cast iron ('Meehanite type')	1	1	1	2	1	3	4	4	2	2	1	1	1	1	1	1	1	2	1
Malleable castings	1	1	1	2	1	4	4	4	2	2	1	1	1	1	1	1	1	1	1
Cast iron	2	1	2	3	2	4	4	4	3	2	1	1	1	1	2	1	1	2	1

Very good 1 Good 2 Medium 3 Poor 4

H_2S) [109, 110] environments and Shih et al [75] have reported that a bright surface is still apparent after 9 years atmospheric exposure.

b) Acids

Chromized steel is resistant to nitric acid and its vapours and no corrosion was observed [53, 75] after 8 months immersion, at ambient temperature, in 15-50% HNO3; in boiling solutions (50%) many items lasted more than 12 weeks without damage. Chromized steels are not suitable for use with hydrochloric or sulphuric acid solutions. Under certain conditions chromized steels can be used in phosphoric acid solutions [78] although in most instances a certain amount of corrosion will occur e. g. a boiling 2% solution resulted in a weight loss of 0.002 i.p.y. [111]. Immersion tests in citric [111] and lactic acid [91, 111] (2-5% solutions at 15-50°C) resulted in corrosion rates of 0.00001-0.001 i.p.y.

c) Alkalies

Chromized steels generally remain unaffected by alkalies e. g. 5% sodium hydroxide at 25oC [89], but severe corrosion may be exposed under strongly oxidizing conditions where the alkaline concentration is greater than 50% and the temperature higher than 100°C.

d) Salt solutions

Immersion tests in distilled-water, [89] tap-water and sea-water [78, 111] have shown that chromized steels exhibit high corrosion resistance to these solutions. After 8 hours testing in a salt spray fog [89] at 35oC chromized steel was less affected than either aluminized steel, galvanized steel or a 17% chromium steel. Very slight corrosion was observed, [53, 91] when immersed in dilute (3%) sodium chloride solutions for 10 to 15 days; the attack was negligible if the surface chromium content was greater than 85% [81-83]. Generally, chromized steels are not considerable suitable for use in chloride solutions or solutions containing free chlorine because of their susceptibility to localised attack under these conditions. Steigerwald [112], from potentiostatic measurements, has concluded that pitting should be negligible if the chromium content at the surface is greater than 30%.

e) Miscellaneous media

Chromized steel sheet in the U.S.A. [92, 98] has

attracted much attention for its potential usage as a material for exhaust gas mufflers. In this respect chromized steel was found to be superior to both aluminized steels and 17% chromium steels [89]. There are some references [113, 114] to the use of chromized steel, in the Russian Chemical Industry, in conjunction with organic media and other solutions (glycol plus sulphuric acid; fatty acids plus linseed oil).

In chromizing, the ultimate chromium concentration that could be obtained is 100% (i. e. equivalent to chromium metal). It is useful, therefore, to consider the corrosion resistance of such material. Wesley has carried out simple immersion tests in acids, alkalies, salt solutions and also under high-temperature conditions, and has tabulated the results of this work [115]. Uhlig comments on Wesley's results and points out that in reducing acids (e. g. sulphuric, hydrochloric etc.) chromium often remains passive for an apreciable period of time until activated at a single point. The entire surface, thereupon, progressively loses passivity dissolving rapidly with evolution of hydrogen.

Chromium is cathodic to steel; economic electrodeposited coatings of chromium are too thin and porous to give protection on their own and are used in conjunction with thick (0.001 in.) deposits of copper or nickel. Chromized coatings on the other hand are relatively thick and can afford protection by their barrier action although corrosion of the steel substrate will be increased at any discontinuities in the coating.

Oxidation resistance

Chromized steel exhibits good oxidation resistance (Fig. 12). It is also resistant to certain other high temperature environments as shown in Table 4.

It is not altogether clear from the literature as to what is the limiting temperature suitable for the use of chromized steel. Other literature [53, 65, 116] is more cautious stating 750°-800°C as the upper limit although temperatures of 800°-900°C may be allowed, intermittently, or if the life expectancy of the item is only of several thousand hours. However, most sources agree that chromized steel has a limited life if used in excess of temperatures of 900°C.

The breakdown of chromized coatings during oxidation has been attributed in part to the phenomenon [117, 118] of secondary diffusion, which decreases the chromium concentration at the metal surface. The mechanism of oxidation is therefore complex [119], although probably similar to that of iron-chromium alloys, a subject reviewed by Wood [120], among others. Protection is therefore dependent on the formation of a coherent barrier scale, or in the case of carbon steels [75, 111] a carbide diffusion barrier [121].

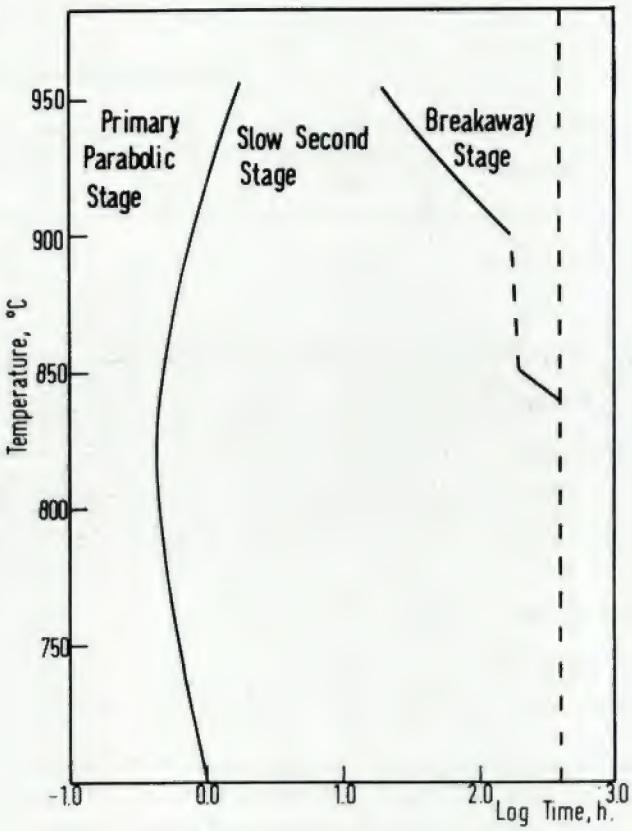

Fig. 12 Oxidation characteristics of chromized iron (118).

ZINC COATINGS

Application methods

Zinc coatings are applied commercially (Table 5) by hot-dipping, electrodeposition, metal-spraying, cementation and vacuum deposition [123-125]. Galvanizing (zinc hot-dipping) has been done for more than 200 years now and it is undoubtedly the most widely used form of metal coating [126]. The production and properties of these coatings has received intensive study over the last 10 years, much of which is reported at the International Conferences on Hot-Dip Galvanizing.

Sprayed-zinc coatings are very similar in nature to their aluminium counterparts but the former are cheaper and are used more at present. The cementation and hot-dip processes used for the application of zinc coatings (i. e. sherardizing and galvanizing) are analogous to the respective aluminium coating processes; a lower temperature is, however, sufficient the diffusion of iron and zinc being significant even as low as 300oC. In this respect, the application of zinc coatings is less expensive, and warpage or loss of mechanical properties of the steel substrate is less likely to occur.

TABLE 5

Methods used for the application of zinc coatings

Method	Temperature (°C)	Thickness (mils)	Deposition rate (mils/h)	Structure of the coating	Remarks
Cementation	350-800	0.5-2	0.3-0.5	Solid solution of zinc in the delta phase	Cementation pack process known as sherardizing
Electrodeposition	20-50	0.1-1	0.2	Essentially pure zinc	
Hot-dip	430-465	1-5	20-50	Outer layer of pure zinc with an interfacial alloy-layer of one or more discrete layers of Fe-Zn compounds	Known as galvanizing; operated on both batch and continuous production
Metal Spray	Ambient	2-20	—	Porous structure (density of approx. 6.32 g/cc)	B.S. 2569

Electrodeposited zinc is readily applied from aqueous electrolytes [122] and with the advent of precoated strip the lower coating thickness and good uniformity are used to their best advantage.

a) Cementation processes

Sherardizing, discovered at the turn of this century [127] is particularly useful for small items where a moderate coating thickness and good dimensional tolerances are required. After cleaning, the articles to be coated, are packed in zinc dust in a metal container, which is then slowly rotated (tumbled) during heatings. Rotation of the drum not only ensures uniformity of the coating but also intimacy of contact. The quality of zinc dust, particularly the iron content, the duration and temperature of heating, affect the nature of the coating produced [128-130]. Generally, temperatures of 350°-375°C are used; this is considerably less than the melting point of zinc (419.5°C). At these temperatures (350°-375°C) a coating of 0.001 in. is formed in about 2 to 3 h. Fig. 13 shows the effect of time and temperature on the rate of formation of coatings by this method. Modifications, aimed at reducing the duration of treatment, have been made by increasing the process temperature up to 450°-850°C [130]. Addition of alumina to the sherardizing powder is necessary to prevent caking. The growth rate decreases with increasing dilution of the reaction powder and it is therefore necessary to optimize the composition of the powder for economic production.

b) Hot-dip processes

Galvanizing is widely carried out by both batch-dipping and continuous dip processes [131]. The steel surface is first prepared by pickling, fluxed, and then immersed in the molten zinc which is maintained at a temperature of about 430°-470°C. The thickness of coating obtained, usually about 0.001-0.004 in.,

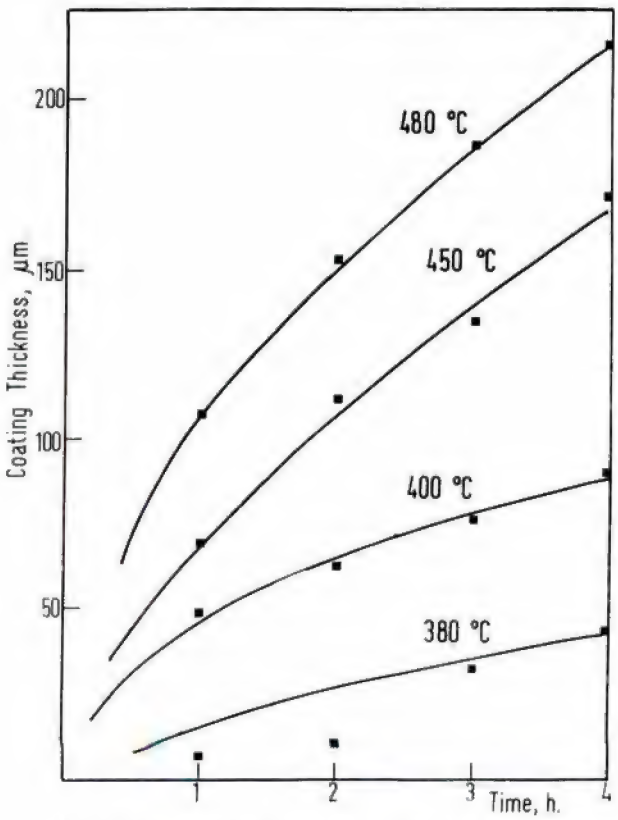

Fig. 13 Zinc cementation coating - effect of process time and temperature on coating thickness (53)

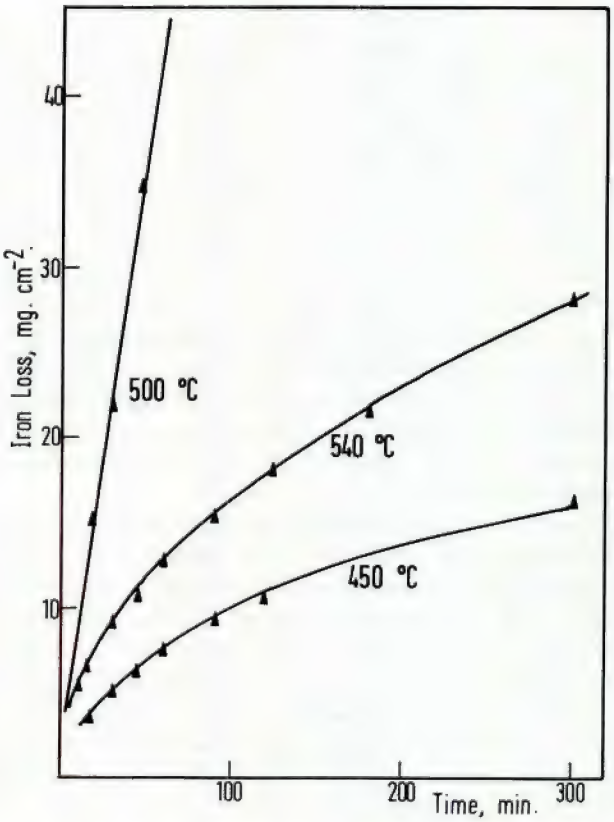

Fig. 14 Hot-dip galvanizing - effect of time on iron loss (i.e. formation of alloy-layer) (170).

depends on the composition of the bath, and process conditions (e. g. time and temperature of immersion, withdrawal speed), the composition, heat capacity and surface profile of the steel. These effects are illustrated by Figs. 14-16. Appart from such major effects as the growth-rate of the alloy-layer and changes in the liquidus temperature there are minor effects observed as a result of alloying additions in the bath. Lead, tin and antimony assist in producing an attractive spangle (a consumer requirement) although antimony also tends to detract from the adherence of the coating and in this respect is similar to cadmium. Aluminium not only inhibits the formation of the alloy-layer but also tends to brighten the surface of the coating. The effect of alloy additions on the production and properties of hot-dipped zinc coatings has been summarized by Rädeker et al [132] and others [133, 134].

At normal galvanizing temperatures alloy growth proceeds at a parabolic rate. A linear relationship is observed as the temperature is increased to within 490°-510°C which reverts to a parabolic growth at higher temperatures (>530°C) (Fig. 15). Galvanizing at abnormally high temperatures (e. g. up to 600°C) has been used for threaded work and also for treatment for steel strip before painting. In both cases the outer zinc layer can be readily removed (centrifuging and wiping, respectively) leaving a thin, uniform coating, wholly of zinc-iron compounds, on the surface.

c) Diffusion heat treatments

The use of coatings comprised solely of zinc-iron alloys may be advantageous for somme applications. The cementation process is limited (by coating thickness obtainable and nature of the article) in its application and heat treatment of hot-dipped or electrodeposited coatings may be used to obtain a thick coating of similar composition. Diffusion of iron and zinc occurs even at temperatures as low as 300oC but temperatures greater than 500oC are generally used for secondary-diffusion heat treatment in order to minimize the treatment time and also to eliminate the zeta phase. In this way the coating is homogenized to some extent which probably increases its cohesive strength and possibly its corrosion resistance. The composition and thickness of these coatings is dependent on the duration and temperature of heat treatment which should be done in an inert atmosphere to minimize the loss of zinc. Gorbunov et al [135] also recommend, in this respect, that the coating should not be greater in thickness, initialy, than 0.004-0.005 in.

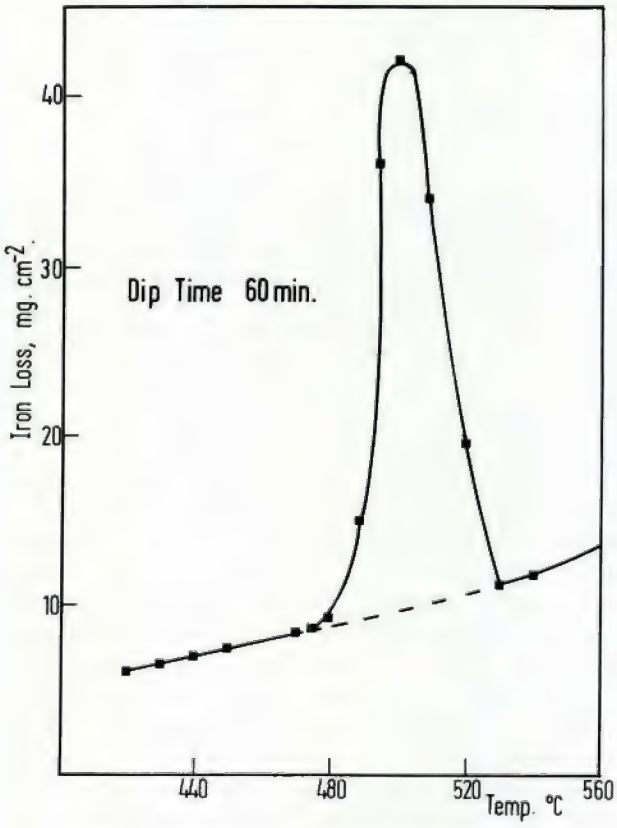

Fig.15 Hot-dip galvanizing - effect of temperature on iron loss (i.e. formation of alloy-layer) (170).

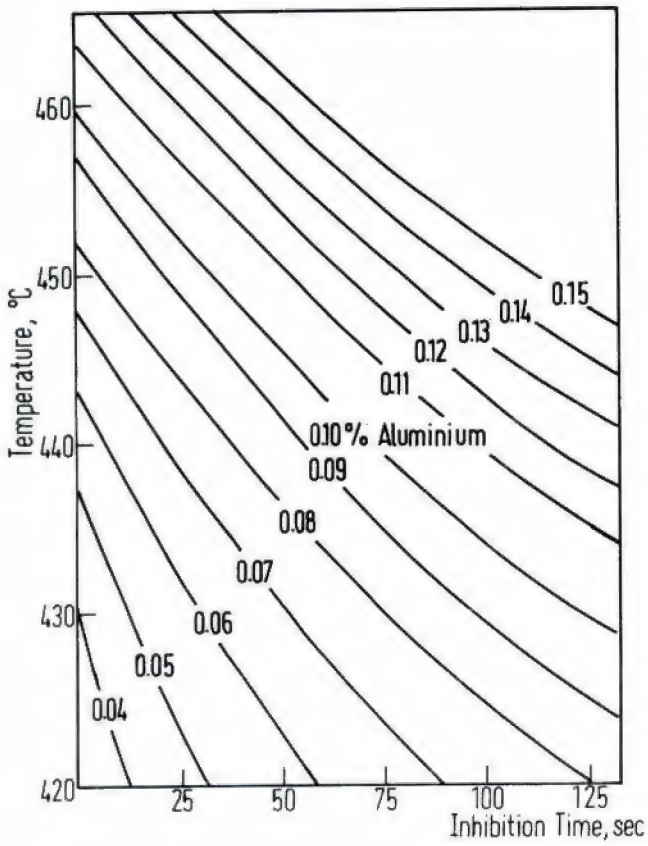

Fig. 16 Hot-dip galvanizing - duration of the inhibitive effect of aluminium on the formation of the alloy-layer (139)

Composition and structure

As a result of the nature of the cementation process, coatings formed therefrom tend to be matte in appearance with a microscopically rough surface. The coating consists in the main of a solid solution of the delta phase ($FeZn_7$) in zinc. Sometimes, particularly at process temperatures higher than 350°C a second layer can be detected at the coating-substrate interface; this appears to be the delta phase. Sherardized coatings produced by the high-temperature processes (500°-800°C) have a greater proportion of the iron-rich phases present; gamma phase (Fe5Zn21) has been detected at the interface. The average iron content of a sherardized coating is about 8-10%; in this respect it is similar to the alloy-layer of conventional hot-dipped coatings. However, coatings produced by the high-temperature cementation methods have higher iron contents often of 15-20%. Because of the brittleness of the zinc-iron compounds and as a result of the difference in expansion coefficients of the coating and the substrate, sherardized coatings tend to contain minute cracks normal to the surface, wich are due to internal stresses.

The normal galvanized coating has a continuous interfacial alloy-layer comprising gamma, delta and zeta ($FeZn_{13}$) phases. A double gamma layer is sometimes observed. Generally the gamma phase contributes less than 5% of the total coating thickness whereas the delta and zeta phases may, together, constitute more than half of the overall coating. The zeta-eta (solid solution of iron and zinc) phase boundary is characterized by its rough uneven form and crystallities of the former are often present in the outer zinc layer. The other phase boundaries, in contrast, tend to be smooth and parallel. The delta phase exhibits a dual structure being relatively coherent with high iron content changing to a fairly course columnar ('pallisade') structure as the iron content decreases.

The zeta phase is not found in coatings produced at temperatures greater than 500oC. At these temperatures the coating contains a layer of coherent delta and an outer region of fragmented delta crystals in a zinc matrix. The structures formed in the linear and upper parabolic ranges differ merely in the degree of fragmentation of the delta phase a thicker layer forming at the higher temperatures. The effects of steel composition have been classified in a similar manner [136]:

i) Normal parabolic - alloy structure similar to that obtained on pure iron
ii) Linear - thin gamma layer next to the steel with a narrow layer of coherent delta phase above which is a region of fragmented delta in a zinc matrix. Above this, and interspersed, are large isolated zeta crystals of pronounced ideomorphic habit (e. g. silicon)
iii) Upper parabolic - broken and porous zeta phase beneath which is a thin delta layer (e. g. high-carbon lamellar pearlitic steels at 459°C)

The surface profile also affects the structure of the alloy-layer; the zeta phase grows normally to the surface resulting in a fan-like structure at convex surfaces (e. g. corners). The thickness of alloy-layer increases with time as does the proportion of delta to zeta. At very short immersion times only the zeta phase can be detected. Of all the bath additions investigated [136, 137] aluminium has the most striking effect and inhibits the growth of the normal alloy-layer [138, 139] by forming a diffusion barrier of Fe_2A_{l5} at the interface; silicon aids this inhibition probably by formation of a ternary alloy. Hershmann [136], among others, has reviewed alloy formation in hot-dip galvanizing.

Physical properties

The application of zinc coatings is generally done at lower temperatures than the other metallic diffusion coatings, and it is unlikely that the mechanical properties of the substrate will be affected providing the process temperature does not exceed 400°C [140].

Iron-zinc compounds are hard and brittle and coatings composed wholly of these alloys, if not cracked already, will withstand little deformation without cracking. Hardness values of iron-zinc alloys have been obtained by several workers [135, 141-144] although those of Jepson et al [143] are not directly comparable because of the nature of the electrodeposited coatings. The values are summarized in Fig. 17. Zinc diffusion coatings produced by heat treatments of both electrodeposited and hot-dipped zinc coatings, consisting largely of the delta phase, crack on more than 5% elongation, [135]. Brittleness, as expected, increases with iron content of the coating and the increased hardness is of value where abrasion resistance is required.

The information on the mechanical properties of hot-dipped zinc coatings is prolific although there appears to be much confusion in the practical interpretation of the results obtained. The adhesion of hot-dipped zinc coatings was found by Horstmann [139] to be determined by both the structure of the coating and also the elongation characteristics of the substrate. Thus, it was shown that a galvanized coating with a thin alloy-layer adheres better if the elongation is high, whilst a coating with a thick alloy-layer adheres more strongly if the elongation is low. Loss of adhesion when it occurred, was always confined to the substrate-alloy (i. e. gamma phase) interface. This is not surprising when the characteristics of the substrate and the gamma phase are compared. Bablik et al [145] have shown by straight pull-off tests (in this respect the test may not be representative of service conditions) that the adhesion of coatings produced from a pure zinc bath is decreased by almost any alloying additions. A series of bending, impact and combined tests have shown [146] that the ductility of galvanized coatings decreases with increasing total thickness of the coating but the thickness of the zinc-iron alloy-layer was less significant. Coatings with zeta crystals in the eta phase tend to be less ductile. Furthermore, Smirnov [147] states that coating strength is secured by a uniform structure and is decreased by the presence of course precipitates or intermediate boundaries between the layers. Applications requiring appreciable formability without flaking or cracking really necessitate the use of aluminium-containing baths although tin endows moderate flexibility.

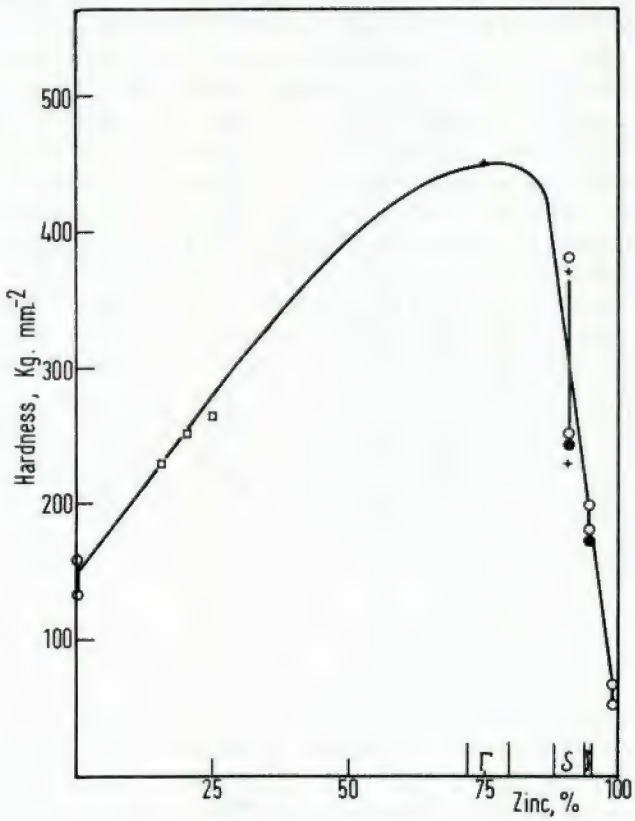

Fig. 17 Hardness of iron-zinc compounds (135, 141, 142, 144) +-(135), o-(141), □-(142), •-(144).

Zinc-coated steel can be welded satisfactorily provided that the correct electrodes are used and the rate of travel is not too fast. Toxic fumes are evolved and crack sensitivity is increased particularly when welding through thick zinc coatings. In a similar manner, depending on the design of the article and the steel composition, embrittlement of steels may occur because of the formation of brittle iron-zinc compounds.

Corrosion resistance

Zinc coatings corrode, generally, in a similar manner to solid zinc, and at any discontinuites in the coating the bare steel is sacrificially protected. The corrosion resistance of zinc to most neutral and slightly alkaline (e. g. pH6-12) media is good. The life of zinc coatings, irrespective of the method of application, has been shown (Fig. 18), [148] in atmospheric environments to be proportional to the weight of applied coating.

Because of the sacrificial actions of zinc, the poor ductility of the coating which may result in cracking, does not deter from the corrosion resistance given by the coating, providing the adhesion is good, although the time to failure will be shortened.

Zinc suffers from a particular form of corrosion known as white-rust; [149] in this respect hot-applied coatings are more resistant than electrodeposited coatings because of the protective layer of oxide

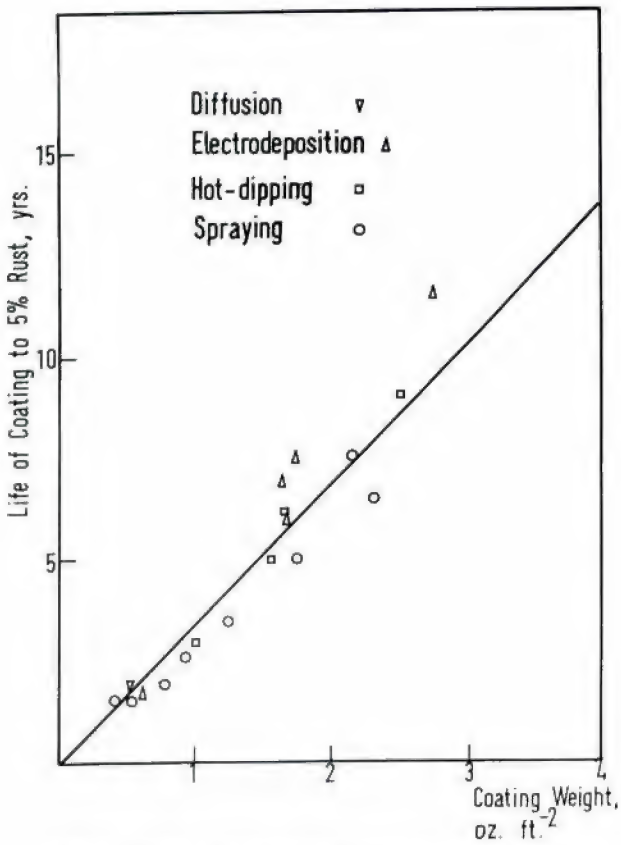

Fig. 18 Lives of zinc coatings exposed to an industrial atmosphere (148)

formed during cooling. The most effective form of protection against this attack is provided by a chromate conversion coating [150].

The corrosion product plays an important role in the corrosion resistance of zinc particularly in aqueous and certain atmospheric environments (c. f. low-alloy or 'watering' steels). In such cases the corrosion rate may be parabolic in nature decreasing with time (c. f. aluminium). Taylor and Tolley [153] examined the characteristics of sprayed-zinc coatings and concluded that the decrease in permeability was related to the extent and type of corrosion (i. e. a function of the pores being stifled by the corrosion products formed therein).

Alloying elements, [132, 137, 154] or impurities, in the zinc coating have been found to have little effect other than that observed by additions of copper or aluminium. The action of copper, which increases the resistance of the coating, is the complete opposite to its effect on aluminium. Aluminium decreases the resistance [155, 156].

The corrosion resistance of zinc-iron alloys and the effect of these alloys on the corrosion resistance of galvanized steel is not, from the literature, entirely clear. These alloys are cathodic to zinc and anodic to steel. An alloy-layer composed of phases can therefore be compared with a duplex (or triplex) nickel-chromium coating where lateral, rather than localised, corrosion is encouraged. Katz [157] attributes the good resistance of heat-treated zinc coatings in waters to the layered structure of the coating. However, because of their iron content the corrosion products from these alloys may be rusty in appearance and may give the premature effect of failure of the coating. Several authorities [135, 157, 158] consider that the zinc-iron phases are more corrosion resistant than pure zinc. Similarly, it has also been found that galvannealed coatings (i. e. galvanized coatings given a diffusion heat treatment at 500° to 600°C) are more resistant to atmospheric corrosion than hot-dipped zinc coatings [159, 160]. The details that were given, are conflicting. Both Higgins [158] and Hadden [159] state that increased corrosion resistance was only observed where the iron content of the coating was greater than 10%. In the latter case the resistance increased with iron content up to 20% the highest concentration investigated. This is in agreement with Katz [157]. Hadden [159] attributed the protection to the formation of black adherent insoluble corrosion products; the protection afforded by these coatings even when damaged, despite the fact that the potential difference between the steel and iron-zinc compounds is less than that between steel and zinc, was still better than the untreated coatings. Reddish corrosion products formed by the iron-rich phases, were found to be less protective. Workers at BISRA [143, 161] also found that the electrodeposited 40/60:Fe/Zn coatings showed an appreciably greater resistance to atmospheric corrosion than other iron-zinc coatings although the interpretation of these results is rendered difficult by the complex nature of the coating which consisted of a heterogeneous deposit of supersaturated alpha phase and gamma phase [162].

Contrary to these results Storey [163] found that sherardized coatings containing 15-20% iron were less resistant to wathering than those containing less. Schueler [164] also exposed galvannealed test pieces but concluded that corrosion resistance increased with iron content up to 8% and although high coating-iron contents could be obtained (e. g. 30%) a value greater than 10% resulted in a decreased corrosion resistance. Sandera and Franz [165] compared the weight loss obtained by immersing iron, zinc, delta zinc-iron and gamma zinc-iron in water over a range of temperature (20°, 60°, and 100°C). They found almost without exception that the corrosion rate of zinc was increased, correspondingly, by the additions of iron (i. e. in decreasing order of resistance (zinc, iron, gamma, delta)). Schramm and Mohrnheim [142] also found that the corrosion rate of zinc-iron alloys (15, 20 and 25% zinc) was greater than either that of iron

or zinc when immersed in a dilute sulphuric acid solution (0.1N). Okamoto and Kaneki [131] carried out tests (in 1% sodium chloride solution) of high-temperature diffusion coatings (iron-rich) and concluded that these coatings were more corrosion resistant than either sherardized or galvanized products. Examination of their results does not, however, show a marked benefit in this respect. The situation is confused further by Hadden [159] who also found that the outer zinc layer and the alloy-layer, of a hot-dipped coating, were similar in their corrosion resistance on exposure to an atmospheric environment.

In conclusion, it would appear that with certain zinc-iron phases present in a coating in a particular structural sequence, enhanced protection (with reference to the present conventional coatings) of a steel substrate can be obtained although the environment too may be fairly specific (c. f. low-alloy steels) in view of the important role played by the corrosion products.

FINAL CONSIDERATIONS

Studies presented in this three part series [121, 171] have shown that diffusion coatings have a useful range of properties, and coatings of zinc (galvanizing) and tin are extensively produced by this process; other diffusion coatings do not appear to have gained wide recognition. In order to increase their field of application future research and development is recommended, namely in the following ways:

1)The process technology of existing, and any newly developed coating systems [172-174]. At present, much energy (in the form of heat) is wasted in the steel industry during hot-rolling. Not only is this energy lost but the formation of millscale takes place. The presence of millscale is generally detrimental to the performance of protective coatings and its removal, before the application of a coating, necessitates the expenditure of further energy. Heat is an essential part of the diffusion process and it would be beneficial if this source, during the production process, could be used for the formation of a metallic diffusion coating. This is realized, in part, by the present cladding and powder processes. It is doubtful whether diffusion rates can be increased significantly except by raising the process temperature; increasing the concentration of non-equilibrium defects (e. g. dislocations) may also be considered. Effort should therefore be concentrated on the efficiency of heating and on increasing the deposition rates. A higher surface concentration will aid diffusion by providing a greater concentration gradient. The use of lower temperatures would be economically beneficial and could probably be offset by the use of vacuum techniques which are more readily available nowadays. It may also be possible to introduce a catalyst into the deposition reaction via either the substrate or the coating metal.

2) Evaluation of new coatings [175]. This is a particularly difficult problem where accurate prediction would be invaluable. Physical properties are fairly readily assessed but the overall performance is often dependent on many factors. The effect of trace elements or additions invoking ternary (or more) behaviour even on the fundamental process of diffusion itself is not yet on a quantitative basis.

3) The parameters affecting the production of protective layers of corrosion or oxidation products [176-179]. The characteristics of the latter are known qualitatively for some systems. This factor with respect to corrosion resistance is a problem applicable to all metal surfaces and will include aspects such as the composition and morphology of the corrosion products themselves, as well as the environment. Considering diffusion coatings, the structure and composition of the alloy-layers, and particularly the potential relationships, will also be participating factors.

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SOME ASPECTS OF NUT FIELD SINGULARITY

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ABSTRACT

Through the study of geodesic deviation, it is observed that the relative acceleration between the neighbouring particles is finite at the singularity of the NUT field.

INTRODUCTION

In an attempt to solve the empty space-time field equations of general relativity, Newman et al (1963) arrived at the Nut metric given by

$$ds^2 = -(1/A)\ dr^2 - (r^2+a^2)\ d\theta^2 + X\ d\phi^2 + 2AY\ d\phi\ dt + A\ dt^2, \qquad (1)$$

where

$A = (r^2-2mr-a^2)/(r^2+a^2)$,

$X = AY-(r^2+a^2)\sin^2\theta$ and

$Y = 4a\sin^2(\theta/2)$.

The metric (1) is singular at

$$r = m \pm (m^2+a^2)^{\frac{1}{2}}$$

It describes the field of a spherically symmetric mass (m) together with a semi-infinite massless source of angular momentum (a) along the axis of symmetry.

Its interesting features have attracted some of the workers (Bonnor (1963) Misner (1963) and Karade (1976)), in the field of the theory of relativity.

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MOTION OF A TEST PARTICLE

The test particle moving in the field (1) follows the time-like geodesic

$$\delta\int\left[-(1/A)\dot{r}^2-(r^2+a^2)\dot{\theta}^2+X\dot{\phi}^2+2AY\dot{\phi}\dot{t}+A\dot{t}^2\right]ds=0 \qquad (2)$$

where dot denotes derivative with respect to s.

The radial motion of the test particle in the plane

$$\theta=\frac{\pi}{2}, \qquad \phi=0$$

is possible (see Karade (1976)) and is given by Euler-Lagrange's equations

$$\ddot{r}-(A_r/2A)\dot{r}^2+(A_rA/2)\dot{t}^2=0 \ and\ \ddot{t}+(A_r/A)\dot{r}\dot{t}=0 \qquad (3)$$

where $A_r = \partial A/\partial r$ etc. Considering (1), these equations after integration yield

$$\dot{r}=\left[A(r_0)-A(r)\right]^{\frac{1}{2}} \quad and \quad \dot{t}=B/A \qquad (4)$$

where the particle is assumed to be at rest at $r=r_0$ and B is a constant given by

$$B=\left[(r_0^2-2mr_0-a^2)/(r_0^2+a^2)\right]^{\frac{1}{2}}=\left[A(r_0)\right]^{\frac{1}{2}} \qquad (5)$$

then for radial motion four-velocity V^i of the test particle takes the form

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$$V^i = \left\{ \left[A(r_0) - A(r) \right]^{\frac{1}{2}}, 0, 0, \left[A(r_0)^{\frac{1}{2}} / A \right] \right.$$

(6)

Considering the space-like triad $U^i_{(\alpha)}$ satisfying the conditions

$$\left.\begin{aligned} & g_{ij} V^i U^j_{(\alpha)} = 0, && (7a) \\ & g_{ij} U^i_{(\alpha)} U^j_{(\alpha)} = -1, && (7b) \\ & \text{and} \\ & g_{ij} U^i_{(\alpha)} U^j_{(\beta)} = 0 && (7c) \end{aligned}\right\} \quad (7)$$

where $i,j = 1,2,3,4$ and $\alpha,\beta = 1,2,3$

Now (7) gives a set of nine equations in U^i_α. We impose three conditions to make the system (7) determinate. Choosing

$$U^2_1 = U^3_1 = U^3_2 = 0$$

one easily obtains

$$U^i_1 = \left\{ \left[A(r_0) \right]^{\frac{1}{2}}, 0, 0, \left[A(r_0) - A(r) \right]^{\frac{1}{2}} / A \right\},$$

(8)

$$U^i_2 = \left\{ 0, 1/(r^2 + a^2)^{\frac{1}{2}}, 0, 0 \right\},$$

(9)

$$U^i_3 = \left\{ 0, 0, 1/(AY^2 - X)^{\frac{1}{2}}, -Y/(AY^2 - X)^{\frac{1}{2}} \right\},$$

(10)

from the system of equations (7).

The equation of geodesic deviation can be written in an invariant form (Pirani (1957), Karade et al (1977)),

$$\frac{d^2 x_\alpha}{ds^2} + K_{\alpha\beta} x_\beta = 0$$

where

$$K_{\alpha\beta} = K_{hijk} V^h U^i_{(\alpha)} V^j U^k_{(\beta)}$$

(11)

The quantity K_{hijk} is the curvature tensor, V^i the four-velocity of the test particle. The quantity $K_{\alpha\beta}$ represents the relative acceleration between the two particles (Karade et al (1977), Tulsani (1981)).

Employing (8)--(11), the straight forward but lengthy calculations give

$$K_{11} = -A_{rr}/2,$$

$$K_{22} = \left[-rA_r/2(r^2 + a^2) \right] + \left[\dot{r}^2 a^2/(r^2 + a^2) + B^2 Y_\theta^2 / 4(X - AY^2) \right] / (r^2 + a^2),$$

$$K_{33} = \left[\dot{r}^2 (X_{rr} - A_{rr} Y^2) / 2(X - AY^2) \right] r^2 - \left[X_r A_r / 4(X - AY^2) \right] + \left[(A_r^2 Y^2 X - B^2 A_r^2 Y^4) / 4(X - AY^2)^2 \right] - \left[\dot{r}^2 (X_r^2 - 2X_r A_r Y^2) / 4(X - AY^2)^2 \right] + B^2 Y_\theta^2 / 4(X - AY^2)(r^2 + a^2),$$

$$K_{12} = 0, K_{13} = 0,$$

and

$$K_{23} = \left[-rBY_\theta (X_r - A_r Y^2) / 4(AY^2 - X)^{\frac{3}{2}} (r^2 + a^2)^{\frac{1}{2}} \right] - \left[\dot{r} B r Y_\theta / 2(r^2 + a^2)^{\frac{3}{2}} (AY^2 - X)^{\frac{1}{2}} \right]$$

All these invariants are regular at

$$r = m \pm (m^2 + a^2)^{\frac{1}{2}}$$

Consequently the relative acceleration of two particles at the singularity of the NUT field is finite.

In the related work of Karade et al (1976) and Karade (1976), the singular surface

$$r = m + (m^2 + a^2)^{\frac{1}{2}}$$

presents a physical barrier. The same conclusion has been arrived at by Rosen (1970) and Hilton (1965) with reference to the Schwarzschild singularity. However these two findings do not contradict each other.

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CONDIÇÃO DE RADIAÇÃO EM MEIOS DE MOVIMENTO

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RESUMO

Apresenta-se uma forma geral da condição de radiação para campos em meios em movimento deslocando-se paralelamente à fronteira.

A equação de onda é obtida no referencial de repouso da fonte fazendo intervir as relações constitutivas para meios em movimento.

A resolução é efectuada introduzindo campos auxiliares e(R) e h(R) e usando uma função de Green diádica.

ABSTRACT

A general form of the radiation condition in moving media is presented.

The wave equation is derived in the rest frame of the source, by using the constitutive relations for moving media.

The equation is solved in terms of a dyadic Green's function and set of auxiliary fields e(R) and h(R).

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I. INTRODUÇÃO

Para fontes em presença de alvos em movimento é usual efectuar a análise no referencial de repouso do alvo, em que as condições fronteiras apresentam a forma mais simples.

Quando a fronteira é constante no tempo é por vezes conveniente resolver o problema no referencial em que a fonte é estacionária.

Esta foi a atitude tomada [2], [3], [5], [6], no estudo de fontes em presença de fronteiras em movimento.

Neste trabalho apresentamos uma forma geral da condição de radiação para meios em movimento.

Embora esta tenha sido considerada implicitamente por certos autores, a sua forma explicita e derivação matemática não foram, tanto quanto sabemos, apresentadas anteriormente.

Consideramos que os meios em presença se deslocam paralelamente à fronteira que os separa.

A resolução é efectuada em termos de campos auxiliares e(R) e h(R) que satisfazem uma equação de onda modificada.

II. EQUAÇÃO DOS CAMPOS

Para meios lineares, homogéneos e isotrópicos em movimento, as equações de Maxwell assumem a forma:

$$\nabla \times \overline{E} = j\omega(\mu\, \overline{\overline{\alpha}} \,.\, \overline{H} - \overline{\Omega} \times \overline{E}) \qquad (1)$$

$$\nabla \times \overline{H} = \overline{J} - j\omega(\varepsilon.\, \overline{\overline{\alpha}} \,.\, \overline{E} + \overline{\Omega} \times \overline{H})$$

em que:

$$\bar{\bar{\alpha}} = a(\hat{x}\hat{x} + \hat{y}\hat{y}) + \hat{z}\hat{z}$$

$$a = \frac{1-\beta^2}{1-n^2\beta^2}$$

$$\bar{\Omega} = \frac{n^2-1}{1-n^2\beta^2}\frac{\beta}{c}\bar{z}$$

(2)

α é uma função característica do meio em movimento.

Definindo dois campos auxiliares pela relação (Tai 1965)

$$\bar{E} = e^{-j\omega\Omega z}\bar{\bar{\alpha}}^{-1} \cdot \bar{e}$$

(3)

$$\bar{H} = e^{-j\omega\Omega z}\,\bar{\alpha}^{-1}\,\bar{h}$$

a substituição de (3) em (1) conduz após alguma manipulação à seguinte equação de onda expressa em função do campo auxiliar e

$$\nabla\times\left[\bar{\bar{\alpha}}^{-1}.\nabla\times(\bar{\bar{\alpha}}^{-1}.\bar{e})\right] - K^2\bar{e} = j\omega\mu\bar{J}e^{j\omega\Omega z}$$

(4)

em que

$$K^2 = \omega^2\mu\varepsilon$$

Esta equação pode ser integrada introduzindo uma função de Green que satisfaz a:

$$\nabla\times\bar{\bar{\alpha}}^{-1}.\left\{\nabla\times\left[\bar{\bar{\alpha}}^{-1}.\bar{\bar{g}}(\bar{R}/\bar{R}')\right]\right\}$$

(5)

$$-K^2\bar{\bar{g}}(\bar{R}/\bar{R}') = \bar{\bar{I}}\,\delta(\bar{R}/\bar{R}')$$

Usando uma forma modificada do Teorema de Green (Tai 1971)

$$\int_V\left\{\bar{\bar{\alpha}}^{-1}.\bar{\bar{g}}(\bar{R}/\bar{R}').\bar{b}.\nabla\times\left[\bar{\bar{\alpha}}^{-1}.\nabla\times\left(\bar{\bar{\alpha}}^{-1}.\bar{e}(\bar{R})\right)\right] - \left[\bar{\bar{\alpha}}^{-1}.\bar{e}(\bar{R}).\nabla\times(\bar{\bar{\alpha}}^{-1}.\nabla\times\times(\bar{\bar{\alpha}}^{-1}.\bar{\bar{g}}(\bar{R}/\bar{R}').\bar{b})\right)\right]\right\}dV =$$

(6)

$$= \oint\oint_S \hat{n}.\left\{\left(\bar{\bar{\alpha}}^{-1}.\bar{e}(\bar{R})\right)\times\left[\bar{\bar{\alpha}}^{-1}.\nabla\times\times\left(\bar{\bar{\alpha}}^{-1}.\bar{\bar{g}}.(\bar{R}/\bar{R}').\bar{b}\right)\right] - \left(\bar{\bar{\alpha}}^{-1}.(\bar{\bar{g}}.(\bar{R}/\bar{R}').\bar{b})\right)\times\left[\bar{\bar{\alpha}}^{-1}.\nabla\times\left(\bar{\bar{\alpha}}^{-1}.\bar{e}(\bar{R})\right)\right]\right\}dS$$

em que b é um vector constante arbitrário e $\hat{n}$ designa a normal interior à superfície fechada S.

De (6) obtém-se:

$$\bar{\bar{\alpha}}^{-1}.\bar{e}(\bar{R}') = j\omega\mu\int_v e^{j\omega\Omega z}\bar{J}(\bar{R}).\bar{\bar{\alpha}}^{-1}.\bar{\bar{g}}.(\bar{R}/\bar{R}')dV +$$

(7)

$$+\oint\oint_S \hat{n}.\left\{\bar{\bar{\alpha}}^{-1}.\bar{e}(\bar{R})\times\left[\bar{\bar{\alpha}}^{-1}.\nabla\times\left[\bar{\bar{\alpha}}^{-1}.\bar{\bar{g}}(\bar{R}/\bar{R}')\right]\right.\right.$$

$$\left.\left.+\bar{\bar{\alpha}}^{-1}.\nabla\times\left[\bar{\bar{\alpha}}^{-1}.\bar{e}(\bar{R})\right]\times\left[\bar{\bar{\alpha}}^{-1}.\bar{\bar{g}}(\bar{R}/\bar{R}')\right]\right\}dS$$

Admitindo que as funções de Green são simétricas verifica-se:

$$\bar{\bar{\alpha}}^{-1}.\bar{\bar{g}}(\bar{R}/\bar{R}') = \left[\bar{\bar{\alpha}}^{-1}.\bar{\bar{g}}(\bar{R}/\bar{R}')\right]^T$$

(8)

$$\bar{\bar{\alpha}}^{-1}.\nabla\times\bar{\bar{\alpha}}^{-1}.\bar{\bar{g}}(\bar{R}/\bar{R}') = \left[\bar{\bar{\alpha}}^{-1}.\nabla\times\bar{\bar{\alpha}}^{-1}.\bar{\bar{g}}(R/\bar{R}')\right]$$

em que T designa o transposto da quatidade entre parenteses.

Substituindo R' por R e fazendo uso das relações de simetria (8), obtém-se, de (7) exprimindo e(R) em função de E(R).

$$\overline{E}(\overline{R})=j\omega\mu\int_v \overline{\overline{a}}^{-1}.\overline{\overline{g}}(\overline{R}/\overline{R}').\overline{J}(\overline{R}')e^{-j\omega\Omega(z-z')}dV' \tag{9}$$

$$+\int\int_S\left\{\left[\overline{\overline{a}}^{-1}.\nabla\times\overline{\overline{a}}^{-1}.\overline{\overline{g}}(\overline{R}/\overline{R}')\right].n\times\overline{E}(\overline{R}')+\right.$$

$$\left.+j\omega\mu\left[\overline{\overline{a}}^{-1}.\overline{\overline{g}}(\overline{R}/\overline{R}')\right].n\times\overline{H}(\overline{R}')\right\}e^{-j\omega\Omega(z-z')}dS'$$

A superfície S pode ser decomposta em duas outras. Uma superfície Sa" cujo raio tende para infinito e uma superfície finita que depende da geometria do problema a tratar.

III.CONDIÇÃO DE RADIAÇÃO

Em meios estacionários, a condição de radiação é, como é bem conhecido dada por (Sommerfeld):

$$\lim_{R\to\infty} R\left[\nabla\times\overline{E}-jk\hat{R}\times\overline{E}\right]=0 \tag{10}$$

Para meios em movimento há que verificar qual a forma que esta condição reveste.

Examinemos de novo a expressão (7) e averiguemos em que circunstâncias é possível considerar que o integral de superfície tende para zero quando R→∞.

De (7) resulta para o integral de superfície

$$\int_{S''}\left[\hat{n}\times\overline{\overline{a}}^{-1}.\overline{e}(\overline{R})\right].\left[\overline{\overline{a}}^{-1}.\nabla\times(\overline{\overline{a}}^{-1}\overline{\overline{g}}.(\overline{R}/\overline{R}')\right] \tag{11}$$

$$-\overline{\overline{a}}^{-1}.\nabla\times\left[\overline{\overline{a}}^{-1}.\overline{e}(\overline{R})\right].\left[n\times\overline{\overline{a}}^{-1}.\right.$$

$$\left..\overline{\overline{g}}(\overline{R}/\overline{R}')\right]dS$$

Se se verificar

$$\lim_{R\to\infty} R\left\{\overline{\overline{a}}^{-1}.\nabla\times\left(\overline{\overline{a}}^{-1}.\overline{\overline{g}}(\overline{R}/\overline{R}')\right)-\right. \tag{12}$$

$$\left.\overline{\overline{A}}.\hat{R}\times\left[\overline{\overline{a}}^{-1}.\overline{\overline{g}}(\overline{R}/\overline{R}')\right]\right\}=0$$

$$\lim_{R\to\infty} R\left\{\overline{\overline{a}}^{-1}.\nabla\times\left(\overline{\overline{a}}^{-1}.\overline{e}(\overline{R})\right)\right.$$

$$\left.-\overline{\overline{A}}.\hat{R}\times\overline{\overline{a}}^{-1}.\overline{e}(\overline{R})\right\}=0 \tag{13}$$

então a condição de radiação é verificada.

Exprimindo os campos auxiliares em função de E(R) e H(R) e atendendo a (9) obtém-se por substituição em (13):

$$\lim_{R\to\infty} Rj\omega\mu\int_V \overline{\overline{a}}^{-1}.\nabla\times\overline{\overline{a}}^{-1}.\overline{\overline{g}}(\overline{R}/\overline{R}')- \tag{14}$$

$$-\overline{\overline{A}}.\hat{R}\times(\overline{\overline{a}}^{-1}.\overline{\overline{g}}.(\overline{R}/\overline{R}').\overline{J}(\overline{R}')e^{j\omega\Omega z'}dV'=0$$

Em espaço livre a função de Green diádica é dada por (Tai 1965)

$$\overline{\overline{g}}(\overline{R}/\overline{R}')=a\left[\overline{\overline{I}}+\frac{1}{K^2a^2}\overline{\overline{a}}.\nabla\nabla\right]g_o(\overline{R}/\overline{R}') \tag{15}$$

em que g_o é um escalar que satisfaz a:

$$(\nabla_a.\nabla)g_o(\overline{R}/\overline{R}')'+K^2ag_o(\overline{R}/\overline{R}')=-\delta(\overline{R}/\overline{R}') \tag{16}$$

em que

$$\nabla_a=\frac{\overline{\overline{a}}.\nabla}{a} \tag{17}$$

Definindo um novo sistema de coordenadas (x_a, y_a, $z_a=az$), para $a>0$ (16) reduz-se à forma usual da equação de onda escalar cuja solução é:

$$g(\overline{R}/\overline{R}')=\frac{ae^{jka^{1/2}R_a}}{4\pi R_a} \tag{18}$$

$$R_a=\left[(x-x')^2+(y-y)^2+a(z-z)^2\right]^{1/2}$$

Como $g_o(R/R')$ satisfaz à condição (12), a equação (13) é verificada também.

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TERMODINÂMICA
uma visão inovadora

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RESUMO

Neste texto *apresentam-se um conjunto de ideias desenvolvidas no âmbito da investigação realizada pelo autor (conceitos fundamentais da Mecânica e Termodinâmica-Clássica e Relativista) e que foram introduzidas no ensino da cadeira de Termodinâmica do Departamento de Física do I.S.T. Estas ideias resultaram, também, de larga experiência de ensino desta matéria e têm-se vindo a afirmar após a escrita do texto "TERMODINÂMICA uma visão inovadora".

- Abordam-se diversos problemas conceptuais, cuja existência e resolução, não são do conhecimento de muitos docentes de Termodinâmica, como se pode facilmente verificar através da consulta da abundante e diversificada literatura neste domínio. Procura-se apenas referir aspectos essenciais podendo-se encontrar na referência 1 o desenvolvimento de muitas destas ideias, aplicadas ao ensino.

Com ligeiras modificações, este texto foi apresentado como relatório nas provas para Professor Associado realizadas no Departamento de Física do I.S.T. em 1987. Em anexo foi apresentado o texto "Termodinâmica uma visão inovadora".

ABSTRACT

This text deals with some ideas developed in the research conducted by the author on fundamental concepts of classical and relativistic Mechanics and Thermodynamics, which have been adopted in teaching Termodynamics at the Physics Department of Instituto Superior Técnico (I.S.T.), Technical University of Lisbon. Such ideas, which were also the outcome of a wide experience in teaching the above discipline, have been more and more firmly established ever since the writing up of the paper entitled "Thermodynamics, a new concept".

Several conceptual problems are approached, whose existance and resolution are unknown to many who teach Thermodynamics, as can be easily concluded from the abundant and varied literature available on the subject. Only essential aspects have been considered, Ref. 1 providing the development of these ideas applied to teaching.

This same text was presented by the author, with slight modifications, under the form of a report, in his examinations for admission to associate professorship, at the Physics Department of I.S.T., in 1987. "Thermodynamics, a new concept", was then included as an annex to the main text.

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1 - A formulação fenomenológica

Um dos conceitos fundamentais da termodinâmica, conjuntamente com o de energia interna é o de entropia, muito embora ainda hoje se encontrem textos onde se apresenta a entropia como uma entidade que culmina um fastidioso e longo percurso histórico formalizado por determinadas propriedades da teoria dos Pfaffianos. Para evitar estas dificuldades num curso introdutório, tem-se vindo a assistir à publicação de numerosos textos em que, numa quase exclusiva visão "estatística", a entropia surge como grandeza associada a um conjunto de cálculos e modelos, que embora interessantes, não são fácilmente relacionáveis com a fenomenologia mais geral do Segundo Principio da Termodinâmica
. Sendo possível uma abordagem fenomenológica que permite introduzir a grandeza entropia associada directamente à essência da termodinâmica, a irreversibilidade, a formulação adquire grande simplicidade e generalidade, e a ligação entre os conceitos de probabilidade termodinâmica e de entropia faz-se com natural complementaridade.

A divisão da física em disciplinas está consagrada e o seu estudo inicia-se com a apresentação da Mecânica Clássica. Esta fica deste modo como se cadeira Mãe fosse e à qual as outras, de certo modo, devessem inibido respeito. Resultam daqui as primeiras dificuldades no ensino da termodinâmica.

Esta disciplina, que tradicionalmente se segue, no curso geral, ao ensino da mecânica, encontra desde logo dificuldades de formulação, dado que colide com o que generalizadamente se ensina em mecânica. De facto, o fenómeno termodinâmico, a irreversibilidade, é tido como não mecânico e se não se fizer a ponte entre a mecânica e a termodinâmica, acaba por se criar no espírito do aluno a sensação de que algo de misterioso e inacessível se passa, existindo até a designação, que pode ser surpreendente para o não iniciado, de mecânica estatística! O conceito de calor surge então como a pretensa entidade essencial e define-se quase universalmente no chamado Primeiro Principio (de uma forma tautológica) como o que falta ao trabalho para dar a variação de energia interna, tautologia essa que contribui ainda mais para acentuar o mistério [2].

Logo na primeira aula procuramos construir uma ideia diferente, incutindo nos alunos que a física é só uma. Para tal sugerimos uma experiência:

A detecção da variação de temperatura de um elástico quando se varia o seu comprimento ou da variação de comprimento, ao variar-se a temperatura. Embora sejam experiências muito fáceis de realizar, é generalizado nos alunos dos primeiros anos de Engenharia o desconhecimento destes factos, e em particular que um elástico aquecido encurte!

A partir desta experiência sugiro e descrevo a possibilidade de se construirem máquinas com elásticos - Archibald Engine [3]. Esta experiência sugere imediatamente que um elástico pode ser esticado sem entrar em "M.O.H.L.S.A." e o seu aquecimento leva a que as equações que habitualmente se escrevem ou são abstracções, dado não conterem este fenómeno, ou então não são da "mecânica".Sugiro que mesmo que o elástico não cedesse ao exterior o "calor" gerado pela extensão, quando abandonado entraria em oscilação amortecida acabando por parar. O mesmo acontece com uma mola!

Formulo então uma pergunta e sugiro a resposta: de que uma mola pára mesmo que não exista ar a perturbar o movimento do corpo que nela se pendurou. Sai-se deste modo do rigor das abstracções e enfrenta-se o rigor revelado por experiências bem simples. Á ideia de que a mola e o elástico páram pelo atrito interno, formulo uma pergunta e dou uma resposta. Esta resposta é habitualmente apresentada como um principio - o "Segundo" Princípio da Termodinâmica. Mas dado ser possível enunciá-lo com grande simplicidade, evitam--se os enunciados tradicionais e de forma equivalente afirma-se que a experiência revela que os sistemas físicos tendem após abandonados a si próprios a definir um estado de equilíbrio que geralmente corresponde á diminuição de amplitude de oscilação. Aceitar que assim é não significa que se compreenda que assim é. De facto, a explicação dos "atritos internos" embora sugestiva não é completamente boa. Para evitar este tipo de explicação considero um modelo "mecânico puro" que é o de um gás de partículas tipo "bola de bilhar" contido num recinto de paredes perfeitamente elásticas. E sugiro várias experiências idealizadas:

Admitamos que o gás ocupa metade de uma caixa em que a outra metade está vazia. Se retirarmos a divisória que separa as duas metades o gás passa a ocupar a totalidade da caixa. À pergunta de se o gás pode voltar a ocupar a metade da caixa a resposta é afirmativa e o tempo que demora a voltar a essa situação depende de uma forma evidente do número de partículas do gás. Torna-se claro que se o número de partículas for muito grande esse tempo também pode ser muito grande, embora para cada condição inicial o problema seja bem determinado. (Faço uma breve referência ao teorema da recorrência de Poincaré).

Seguidamente sugiro outra experiência realizada com o referido gás. O gás está confinado agora a um volume imposto por um êmbolo e as colisões são elásticas. As partículas colidem com o êmbolo e por

isso, no ínicio, equilibram o peso do êmbolo. Se se acrescentar uma massa M ao êmbolo este desce, e é de admitir que possa voltar à posição e velocidade iniciais(.4) Sugere-se que da mesma forma que no modelo anterior (embora aqui seja menos evidente que assim é) o tempo que demora o gás e o êmbolo a regressar ao estado inicial (posição no espaço de fase) depende do número de partículas que constituem o gás (Ciclo de Poincaré). Embora as equações sejam deterministas, aderem à "tirania dos grandes números". Apresento para caracterizar melhor a ideia um transparente do Hexstat [5]. É esta a ideia do fenómeno termodinâmico, ideia que ultrapassa o domínio da Termodinâmica dado aderir a uma interprestação estatística.

Seguidamente introduz-se a variável entropia[6]. Para tal, aceita-se como evidente que a pressão exercida por um gás é uma função crescente com a densidade de energia [6]. A aceitação do equilíbrio implica que U=U(S,V) - (Este modelo pode ser desenvolvido com um elástico). Deste modo o equilíbrio e a entropia surgem de imediato e a futura ligação com a interpretação estatística está lançada. Pode arbitrar-se numa transformação irreversível $\Delta S>0$. A reversível é tal que $dS=0$. O longo percurso histórico que levou ao conceito de entropia é completamente ultrapassado.A noção de trabalho apresentada tem um sentido físico evidente, dado corresponder à variação de energia potencial gravitacional (Gibbs, Pauli). O conceito de calor é identificado com o de energia interna [2,7]. Deste modo o princípio da energia-entropia ("Segundo" Princípio) enuncia-se de forma original afirmando que quando um Sistema [7] regressa à configuração inicial houve transformação de trabalho em calor, isto é, há pesos que descem e o sistema aumenta de energia e por isso aquece. Tal facto deve-se à assimetria que pode ser explicitada na "força" que no modelo do gás este exerce sobre o êmbolo obtida a partir de $p=\alpha u$[8] e do "efeito Doppler" (A one dimensional model of irreversibility, trabalho desenvolvido no grupo 4 do CEL [4]). Mas nesta fase da exposição, para alcançar generalidade e simplicidade, apenas se salienta que o equilibrio implica a assimetria de conversão de trabalho em calor. Vários exemplos práticos são apresentados e em particular sublinhada a componente ecológica de grande actualidade e importância. È nesta fase da exposição que é feita a ponte com o passado e se apresentam de uma forma evidente os enunciados de Clausius, Kelvin, Planck e Carnot, reduzidos a grande simplicidade dado o poder de síntese que a formulação inovadora apresentada permite alcançar. (em relação ao trabalho de Carnot é sempre motivo de curiosidade a afirmação de que a sua analogia com a máquina hidráulica funcionou e funciona bem, mesmo sem conservação do calórico [2]!).

O conceito de temperatura surge como um conceito ligado ao equilibrio ("Segundo" Principio) dado que ao longo de uma superfície

$$U=c,^{te}S=c^{te} \quad , \quad \frac{\partial U}{\partial S}=c^{te} . \quad [2][9]$$

Desde que bem introduzido o conceito de fonte como limite de um sub-sistema finito [6], é pedagógico e não escamoteia o "Segundo " Principio [9].

Numa tranformação feita ao longo de pontos de equiliíbrio fisicamente próximos temos

$$dU=<dU,dP>=\left(\frac{\partial U}{\partial S}\right)_{x_k} dS+\left(\frac{\partial U}{\partial x_K}\right)_S dx_K$$

em que se usa a convenção de Einstein em K e sendo dU a diferencial exterior de U, dP um deslocamento elementar entre dois pontos próximos e $< dU, dP>$ a contracção da forma dU e do vector dP [10].

$$Se \quad dS=0, dU=\left(\frac{\partial U}{\partial x_K}\right)_S dx_K=-p_K dx_K=dW$$

onde dW é o trabalho elementar nesse deslocamento. Deste modo não se confunde (o que é generalizado) tranformação quase-estática com reversível e o trabalho só é evidentemente $-p_K dx_K$ numa reversível [2,6,7,9] (a confusão sobre este assunto é generalizada e está na base de falsas interpretações nos mais diversos domínios).

Temos portanto que $dU = -p_K dx_K + TdS$ é uma igualdade válida numa transformação quase-estática de um Sistema [8].

Para o Sistema e numa reversível $dS = 0$ e $dU=-p_K dx_k=dW$. Numa irreversível temos que a variação de entropia do sistema é maior que zero (arbitrou-se $\Delta S>0$) e portanto

$$T=\frac{\partial U}{\partial S}>0 \quad .$$

A concepção globalizante de Sistema e o trabalhar-se com Sistemas finitos permitiu este esclarecimento. Não se recorre ao "Primeiro" Princípio ficando ultrapassadas as classificações de "Primeiro" e "Segundo" aliás de acordo com a cronologia histórica dos trabalhos de Carnot e Joule.

A apresentação do gás ideal é feita através da equação $p=\alpha u$. Mostra-se que $p=\alpha u$ e a tendência para o equilibrio que implicitamente [4] lhe está associada contem toda a informação termodinâmica do sistema [8]. Surge uma nova e distinta classificação de gás ideal clássico (como um limite de

"Bose-Einstein" e "Fermi-Dirac") a partir de $p=\alpha u$ [8]. Fenomenologicamente atinge-se um resultado consistente com a análise que na formulação estatística irá também ser obtido através das estatisticas de Bose-Einstein e Fermi-Dirac.

Terminam-se os aspectos essenciais da formulação fenomenológica chamando a atenção para a síntese contida no quadrado termodinâmico [1]. A relação entre grandezas fundamentais e parâmetros mensuráveis é feita através das relações de Maxwell. [O facto de a temperatura se medir directamente o mesmo não acontecendo com a entropia criou a dificuldade de evidenciar esta grandeza e a que fosse necessário um longo percurso para se obter a relação fundamental $U=U(S, x_k)$ 1,6].

2 - A formulação estatística

A formulação estatistica é feita na segunda parte do curso.

De uma forma consistente com a apresentada na primeira parte, a ideia de equilíbrio é tida como fundamental. Se é fácil para o aluno compreender a expansão livre de um gás (a expansão livre faz-se a energia constante) no espaço das posições (x,y,z) já se torna no entanto mais difícil de prever a evolução do gás no espaço das velocidades (v_x, v_y, v_z).

Com o objectivo de caracterizar fisicamente este problema proponho o seguinte modelo:
Um feixe monocinético é introduzido numa caixa, confinado a um ângulo sólido $d\Omega$.

As partículas do feixe estão incialmente confinadas a um elemento de volume no espaço das velocidades. Admitindo apenas colisões elásticas é fácil compreender que as colisões das partículas com as paredes e entre si levam a que estas saiam do elemento de volume por alteração de direcção e de módulo. É levantada então a seguinte questão:

Qual será a função de distribuição de velocidades das partículas? Será possível prever uma situação final de equilibrio que eventualmente se estabeleça? A resposta a esta pergunta foi dada por Maxwell e Boltzmann mas antes de se obter essa resposta introduzo através de um modelo muito simples a ideia e o método de Boltzmann:

- Num tabuleiro a duas dimensões imagino uma fotografia construída por partículas localizadas em macrocélulas e microcélulas. À ideia de microestado e macroestado associo a ideia de cópias diferentes de uma mesma fotografia e apresento um transparente com uma fotografia processada por computador [11]. A pergunta equivalente à pergunta difícil de Maxwell relativa às velocidades é aqui formulada relativamente à distribuição de partículas no tabuleiro. Se o tabuleiro começasse a vibrar, ou melhor ainda, se as partículas estivessem animadas de velocidade e não existisse atrito com o tabuleiro e as colisões com as paredes fossem elásticas, que distribuição de partículas se observaria no espaço das posições? Esta situação final depende da figura inicial? A resposta a esta pergunta, que é fácil, sugere a introdução da estatística na previsão destas situações "finais" ditas de equilíbrio. Para tal abordo uma ideia muito geral sob o título sugestivo e bem conhecido da "ordem" que surge do "caos". Utilizo o "Hexstat" que permite introduzir a distribuição binomial associada ao número de caminhos das bolas que são lançadas do tôpo e que acabam por caír em diversos compartimentos, dando lugar a uma curva que é previsível com uma dada incerteza. A curva tende, quando o número de bolas é muito elevado, para a curva de Laplace-Gauss. Feitos vários lançamentos das bolas com condições iniciais que não são rigorosamente as mesmas verifica-se que a forma que define uma "ordem" e cuja expressão matemática é bem conhecida não depende de uma descrição pormenorizada das trajectórias das partículas. É esta "tirania dos grandes números" que permitirá resolver o problema de Maxwell. O modelo associado ao "Hexstat" serve para apresentar conceitos fundamentais de estatística e é relacionado com o random walk, com o paramagnetismo e com as leis de difusão (cada um destes fenómenos físicos é depois abordado em pormenor).

Associados os conceitos de microestado, macroestado, equilibrio e probabilidade termodinâmica apresenta-se a ideia de Boltzmann de relacionar a probabilidade termodinâmica com a entropia baseada no facto de o número de microestados de um sistema só poder aumentar (assimetria). Para o modelo do tabuleiro calcula-se a probabilidade termodinâmica de um macroestado no caso de partículas indiscerníveis. Dado ter-se admitido que $S=S_1+S_2$[9] e que S é uma função crescente de W faz-se $S=K\ell nW_{total}$, sendo possível para um grande número de partículas fazer assimilar S a $K\ \ell n\ W_{max}$ onde W_{max} é a probabilidade termodinâmica associada ao macroestado $\{n_j\}$ que maximiza a probabilidade termodinâmica $W\{n_j\}$. Embora esta hipótese seja razoável e tenha fácil aceitação por parte dos alunos, indico que ela pode ser demonstrada analiticamente, isto é, que é possível atingir resultados equivalentes considerando W_{total} [12]. Esta hipótese corresponde a afirmar que os valores médios observados para todos os $\{n_j\}$ são os mesmos de $\{n_j\}_{max}$ ou a admitir a equiprobabilidade dos microestados de igual energia. A ideia de que o equilibrio apenas corresponde a $\{n_j\}_{max}$ é assim claramente analisada evitando-se as contradições que uma apresentação aligeirada geralmente induz. Deste modo não há paradoxo de recorrência de Poincaré [4]. A maximização de $W\{n_j\}$ no caso do tabuleiro é apresentada como exemplo simples do método que depois é estendido ao espaço

de fase feitas as contagens de $W\{n_j\}$ de acordo com Bose-Einstein e Fermi-Dirac.

O gás ideal clássico é obtido como limite destas duas estatísticas (B.E. e F.D.) para um número de ocupação médio das microcélulas muito inferior à unidade.

Mostra-se que este mesmo resultado pode ser obtido se as partículas forem consideradas discerníveis e é independente da condição $N_j << 1$. Este é o caso de sistemas quânticos localizáveis, facto para o qual se chama a atenção, relacionando-o de uma forma fácil com o método de Gibbs das cópias mentais. Como exemplo dá-se o modelo do paramagnetismo

Após se mostrar que

$$dU = \beta^{-1} d\ln W + \Sigma \overline{N}_i du_i$$

para as estatísticas de B.E. e F.D, associamos T dS a β^{-1} $d\ln$ W e $X_k dx_k$ a ΣN_i du_i, tendo admitido que $S=f(W)$. Obtemos com independência do Primeiro Princípio, $S=K\ell nW$ e $\beta^{-1}=KT$[2,13]. É deduzida a equação de Sackur-Tetrode para um gás ideal (no sentido de $p=\alpha u$) no limite clássico ($N_i << 1$). A partir da equação Sackur-Tetrode interpreta-se de uma forma original o "Segundo" Princípio [14]. Para a estatística de Maxwell-Boltzmann obtem-se a função de distribuição de velocidades. Um segundo exemplo de equilibrio no espaço das posições é abordado para um gás num campo gravitacional. Este exemplo é particularmente interessante, pois serve para mostrar que também no espaço das posições, o "caos" pode estar ligado ao aparecimento de estruturas, ideia que actualmente se tem vindo a impor contrariando a de morte térmica.

A Termodinâmica tem hoje na Engenharia, particularmente, e este é um exemplo notável, no domínio da análise energética de sistemas através do método da exergia, método recente e em que se visa o importante objectivo do aproveitamento óptimo da energia, tem hoje sem dúvida um papel de grande relevo. No entanto possui implicações que ultrapassam em muito esse papel. Por esse motivo, e como se refere na introdução de [1] há que pensá-la como formativa de modo a abrir perspectivas no espírito dos alunos. Já não se trata da ciência do "calor"* mas sim da ciência que estuda a evolução dos sistemas. A entropia deve ser evidenciada como uma grandeza essencial e não surgir como mera curiosidade para estudiosos [3,15,16].

*Com esta afirmação pretende-se chamar a atenção para o caracter não essencial do "primeiro princípio" dado a formulação poder ser feita através do conceito de energia interna [2, 7, 5, 6]. De uma forma, em grande parte, consistente com esta ideia foi recentemente publicado um artigo [17].

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